

BENZO[*b*]TELLUROPHENE, DIBENZO[*b,d*]TELLUROPHENE, AND THEIR DERIVATIVES. (REVIEW)

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*Data on the synthesis, reactions, crystal structure, and spectral characteristics of benzo[*b*]tellurophene, dibenzo[*b,d*]tellurophene, and their derivatives are reviewed and analyzed.*

Keywords: benzo[*b*]tellurophene, dibenzo[*b,d*]tellurophene, cyclization.

Tellurophene and its derivatives have unique reactivity in comparison with other five-membered heteroaromatic compounds and have therefore attracted considerable attention. Detailed reviews have been devoted to their synthesis and transformations [1, 2]. At the same time the benzannelated derivatives (benzo[*b*]tellurophenes and dibenzo[*b,d*]tellurophenes), methods for the production of which are examined in the present review, have been studied to a significantly lesser degree. Of the five-membered heterocycles containing one tellurium atom dibenzotellurophene was synthesized first [3], while the first representatives of tellurophenes and benzotellurophenes, i.e., tetraphenyltellurophene [4] and 3-chloro-2-phenylbenzo-*[b]*tellurophene [5] respectively, were obtained much later.

1. BENZO[*b*]TELLUROPHENE

In contrast to its chalcogen analogs benzo[*b*]selenophene and particularly benzo[*b*]thiophene, benzo[*b*]tellurophene (**1**) and its derivatives have been studied insufficiently [1, 2, 6]. Although a paper on the synthesis of one member of this series, i.e., 3-oxo-2,3-dihydrobenzo[*b*]tellurophene (telluroindoxyl) appeared in 1928 [7], it proved erroneous [8, 9]. The first reliably described representative of benzo[*b*]tellurophenes is probably 3-chloro-2-phenylbenzo[*b*]tellurophene, which was obtained in 1971 [5].

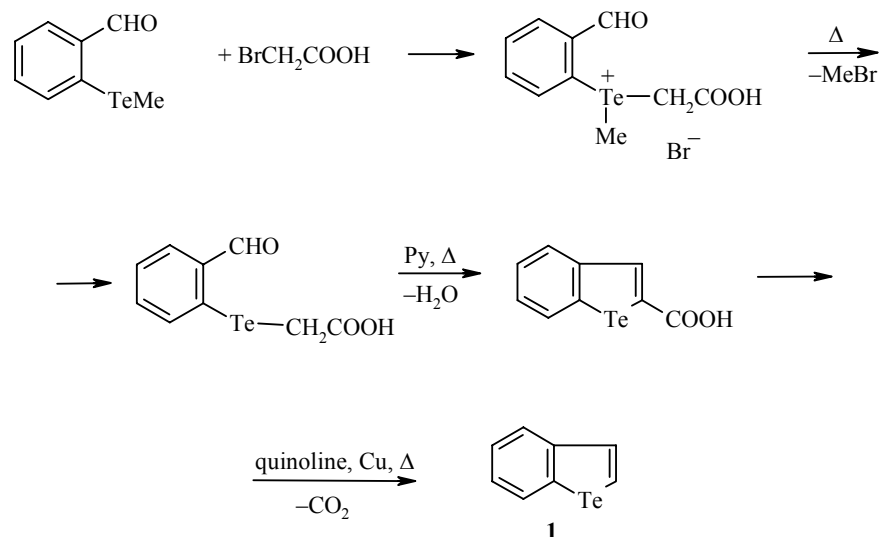
1.1. Synthesis of Benzo[*b*]tellurophene and Its Derivatives

Methods for the synthesis of benzo[*b*]tellurophene (**1**) and its derivatives from noncyclic organotellurium compounds can be divided into two main groups according to the method of closure of the tellurophene ring and the structure of the initial substances. The first group includes the cyclization of C₍₂₎-C₍₃₎ and C₍₂₎-Te of carbonyl(vinyl)-substituted benzenes, containing a TeR group (R = CH₂Y, where Y is an electron-withdrawing substituent) or TeMeBr₂ group at the *ortho* position. 2-Substituted benzo[*b*]tellurophenes

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are mainly formed as a result of these reactions. The second group of methods involving Te-C_{arom} cyclization, which lead to 3-halobenzo[*b*]tellurophenes, are based on the use of the comparatively readily obtainable (2-phenylvinyl)tellurium trichlorides PhCR²=CR¹TeCl₃. These reactions are specific to the chemistry of benzo[*b*]tellurophenes, in so far as the selenium and sulfur analogs of the above-mentioned σ-telluranes are unstable.

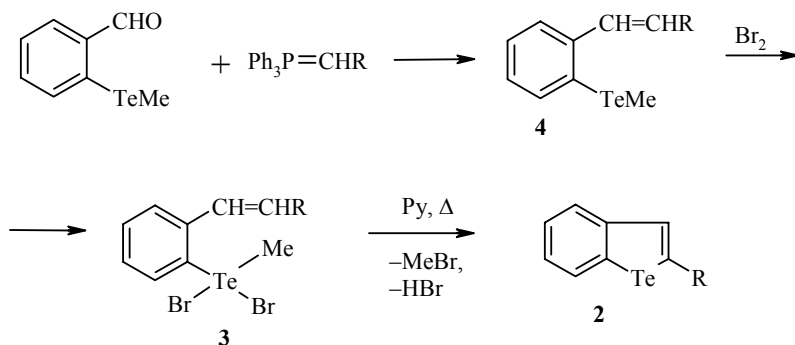
The first benzo[*b*]tellurophene (**1**) was obtained by a four-stage synthesis [9] from *o*-(methyltelluro)benzaldehyde [10] and bromoacetic acid. The overall yield of the product **1** amounted to 54% (calculated on the initial aldehyde).



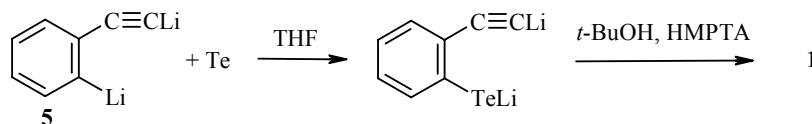
2-Acetylbenzo[*b*]tellurophene was synthesized from the same aldehyde and bromoacetone in a similar way with an extremely low yield [11].

Low yields of 2-substituted 3-methylbenzo[*b*]tellurophenes were obtained in the reaction of *o*-(methyltelluro)acetophenone [12] and bromides BrCH₂R [11, 13]. Thus, the yield of 2-carboxy-3-methylbenzo[*b*]tellurophene amounted to 10% [13].

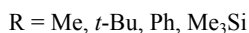
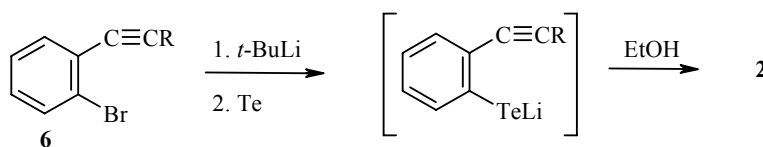
Another approach to the production of 2-R-benzo[*b*]tellurophenes **2** was based on the intramolecular cyclization of substituted styrenes **3** by boiling in pyridine [11]. The initial *o*-(methyltelluro)styrenes **4** for the synthesis of compounds **3** were obtained with high yields by the Wittig reaction of *o*-(methyltelluro)benzaldehyde with stabilized phosphoranes. Oxidation of the tellurides **4** with bromine leads to the products **3** with almost quantitative yields. However, it was not possible to obtain 2-formylbenzo[*b*]tellurophene by this method.



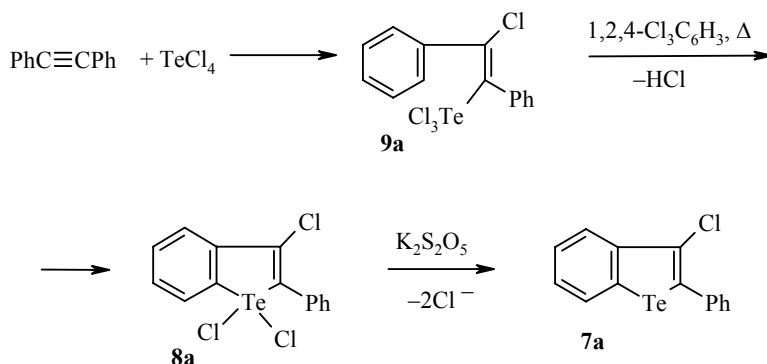
Derivatives of lithioacetylenes are promising for use in the synthesis of benzo[*b*]tellurophene **1** and its substituted derivatives **2**. Thus, compound **1** was obtained with a yield of 85% by the reaction of the lithium derivative **5** with Te powder in THF followed by treatment of the obtained lithium tellurolate with a mixture of *t*-butyl alcohol and HMPTA [14].



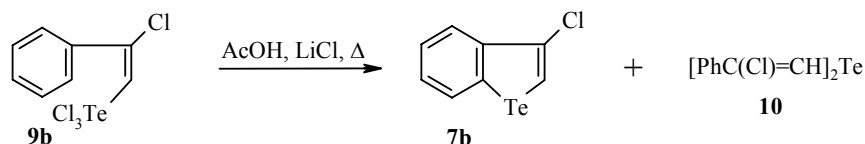
o-Bromoethynylbenzenes **6**, synthesized with yields of 78-93% by the coupling of *o*-bromoiodobenzene with substituted acetylenes $\text{RC}\equiv\text{CH}$ catalyzed by $\text{PdCl}_2(\text{PPh}_3)_2$, were used for the production of 2-*R*-benzo[*b*]tellurophenes **2**. The required products **2** were obtained with yields of 45-74% by treating compounds **6** with *t*-butyllithium and with tellurium and then adding ethanol to the reaction mixture [15].



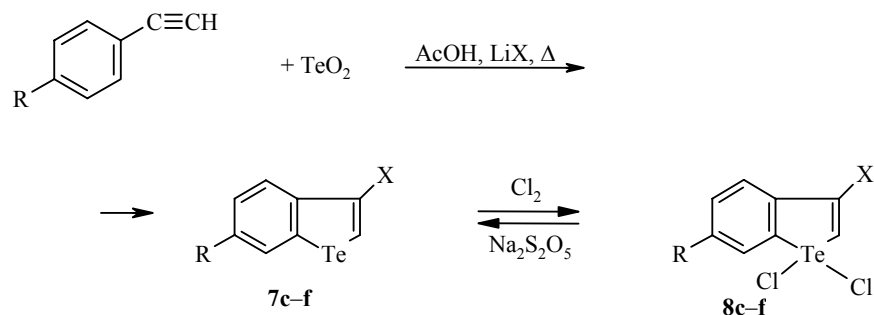
3-Chlorobenzo[*b*]tellurophenes **7** were synthesized by the intramolecular electrophilic cyclization of β -chlorostyryltellurium trichlorides. The first representative of the series – 3-chloro-2-phenylbenzo[*b*]tellurophene (**7a**) – was obtained with an almost quantitative yield by the reduction of 1,1,3-trichloro-2-phenylbenzo[*b*]tellurophene (**8a**) [5]. The latter was in turn obtained with a yield of more than 50% by heating α -phenyl- β -chlorostyryltellurium trichloride (**9a**) [16].



It should be noted that attempts at thermal cyclization of the trichloride **9b** were unsuccessful. However, when this compound was boiled in acetic acid in the presence of lithium chloride the 3-chlorobenzo[*b*]tellurophene **7b** was obtained with a yield of 38% together with bis(β -chlorostyryl) telluride **10** [17].

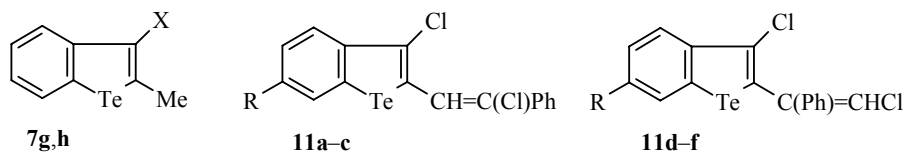


An extremely convenient preparative method for the production of 3-halobenzo[*b*]tellurophenes, not requiring the prior synthesis of vinyltellurium trichlorides of type **9**, was developed by Bergman [17, 18]. Compounds **7c-f** were obtained with yields of 21-92% by the reaction of arylacetylenes with TeO₂ in acetic acid in the presence of an excess of LiX (X = Cl, Br, I). The products were purified by conversion into the corresponding 1,1-dichlorobenzotellurophenes **8**, crystallization of the latter, and reduction.



7, 8 c R = H, X = Br; **d** R = H, X = I; **e** R = Me, X = Cl; **f** R = Br, X = Cl

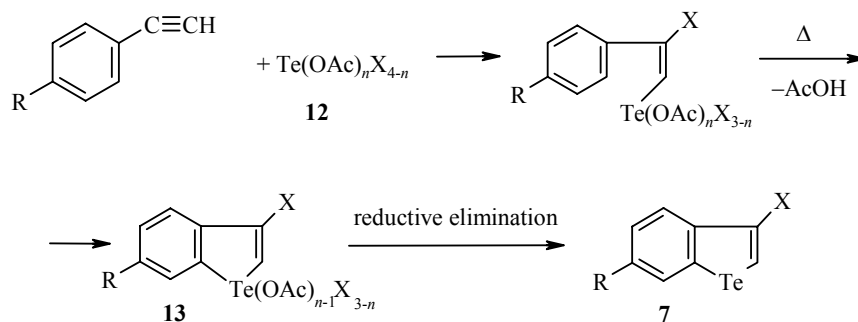
Certain disubstituted acetylenes enter into a similar reaction. Thus, the benzo[*b*]tellurophenes **7g,h** were synthesized with yields of 28 and 49% respectively from 1-phenyl-1-propyne under conditions similar to those described above [17]. However, heterocycles of type **7** were not obtained from diphenylacetylene and 1,4-diphenyl-1,3-butadiyne.



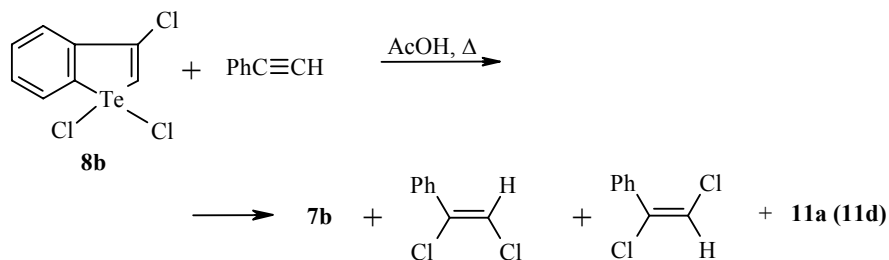
7 g X = Cl, **h** X = Br; **11 a, d** R = H, **b, e** R = Me, **c, f** R = Br

It should be noted that compounds **11a-c** or **11d-f** are also formed in addition to the products **7** if lithium chloride is used as source of halogen [17].

A possible mechanism for the reaction includes electrophilic addition of the intermediate tellurium halide acetates **12** (the structure of which was not accurately established) at the triple bond of the acetylenes followed by ring opening and reductive elimination of the σ-telluranes **13** [17, 18].



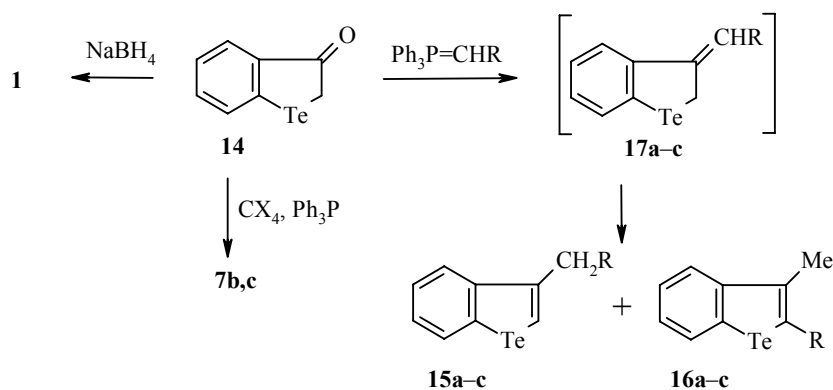
To judge from the behavior of various derivatives of the R_2TeX_2 type spontaneous elimination of electronegative substituents from σ -telluranes **13** is unlikely. Such a process obviously takes place under the influence of compounds present in the reaction mixture. In fact, when the tellurium dichloride **8b** is boiled with phenylacetylene in acetic acid 3-chlorobenzo[*b*]tellurophene **7b**, a mixture (95:5) of the *Z*- and *E*-isomers of 1,2-dichloro-1-phenylethylene, and a certain amount of compound **11a** or **11d** are formed [17].



It should be noted that compound **7c** was also obtained by boiling acetophenone semicarbazone with TeO_2 in acetic acid in the presence of lithium bromide [17]. It is clear that the TeO_2 , like SeO_2 [19], oxidizes the semicarbazone to phenylacetylene, which reacts as described above. However, the yield of 3-bromobenzo[*b*]tellurophene (**7c**) amounts to only 9%, while the semicarbazones of other ketones do not react at all [17].

Benzo[*b*]thiophene and benzo[*b*]selenophene (yields 85 and 40% respectively) were synthesized by high-temperature reaction of diphenyl dichalcogenides with acetylene [20]. However, in the case of diphenyl ditelluride under the same conditions the yield of benzo[*b*]tellurophene (**1**) amounted to only 1-2%.

Benzo[*b*]tellurophene **1** and a series of its derivatives were synthesized from compounds containing five-membered tellurium-containing cyclic fragments. In particular, the product **1** was obtained with a 20% yield from the telluroindoxyl **14** (see section 1.3) by reduction with sodium borohydride [21]. Treatment of compound **14** with tetrahalides CX_4 ($X = Cl, Br$) in the presence of triphenylphosphine gave 3-halobenzo[*b*]tellurophenes **7b,c** with yields of 25 and 30% respectively [13]. The 3-substituted compounds **15a-c** were obtained from telluroindoxyl **14** by the Wittig or Wittig-Horner reaction [13]. Here the isomeric compounds **16a-c** were formed in addition to the products **15a-c**. The ratio of the isomers depended on the nature of the employed phosphorane and on the reaction conditions. The reaction probably takes place through the intermediate **17**, which undergoes either a sigmatropic 1,3-hydrogen shift, leading to the products **15**, or a 1,3-sigmatropic tellurium shift with the formation of the product **16** [13].

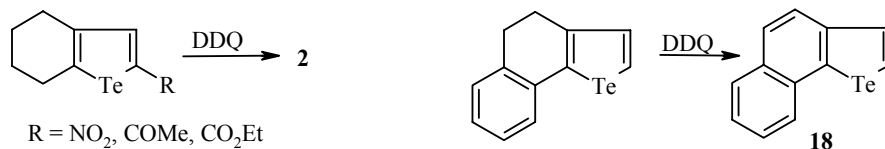


15-17 a R = CN, b R = COMe, c R = CO₂Et

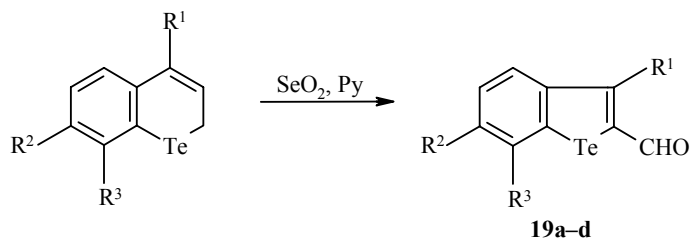
Such rearrangement is specific to telluroindoxyl and does not occur in the case of its sulfur and selenium analogs.

With the use of telluroindoxyl in the Wittig–Horner reaction it is possible to employ lower temperatures and to reduce the amount of isomerization products **16** [13]. Thus, compounds **15a,c** were synthesized with yields of 80 and 55% respectively.

Aromatization by the action of dichlorodicyanobenzoquinone (DDQ) was used for the production of certain benzo[*b*]tellurophenes of type **2** and naphtho[1,2-*b*]tellurophene **18** [22].



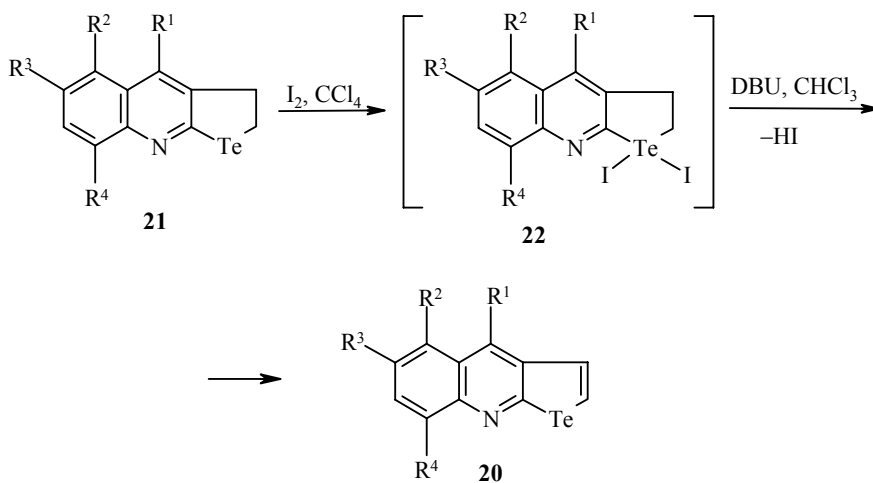
Tellurochromenes were used for the synthesis of 2-formylbenzo[*b*]tellurophenes **19a-d**. Oxidation of the tellurochromenes by selenium dioxide is accompanied by ring contraction, leading to the aldehydes **19a-d** with yields of 25-60% [23, 24].



a R¹ = R² = R³ = H; **b** R¹ = Me, R² = R³ = H; **c** R¹ = R³ = H, R² = Me; **d** R¹ = R² = H, R³ = Me

The aldehyde **19a** was also obtained when K₂Cr₂O₇ was used as oxidizing agent [25].

The initial compounds **21** for the synthesis of telluro[2,3-*b*]quinolines **20** were oxidized to the diiodides **22**, but the latter were not isolated but were used *in situ*. When 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used as base the yields of the heterocycles **20** were relatively low (18-35%) [26].



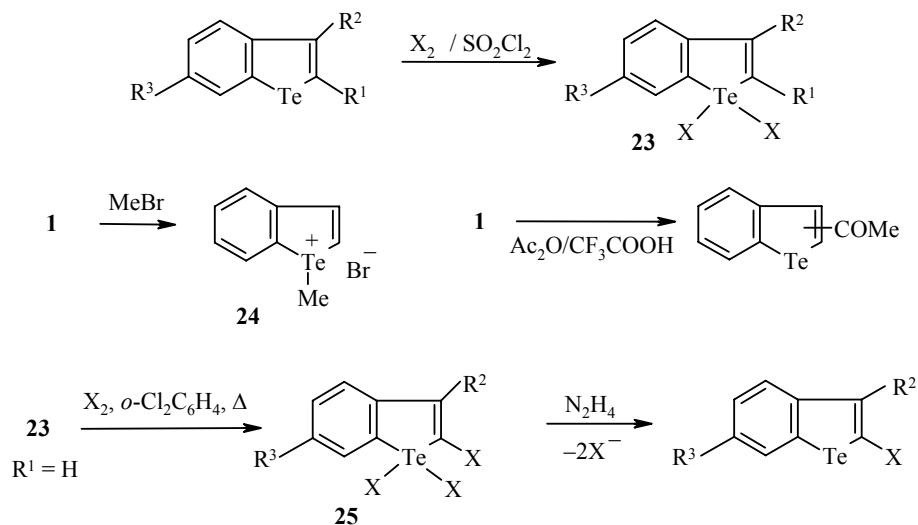
R¹ = R² = R³ = R⁴ = H; further indicated R ≠ H: R⁴ = Me; R² = R⁴ = Me; R³ = Cl; R¹ = Ph

1.2. Reactions of Benzo[*b*]tellurophene and Its Derivatives

Like other derivatives of dicoordinated tellurium, benzo[*b*]tellurophene is oxidized by halogens or SO_2Cl_2 under mild conditions to the 1,1-dihalides **23** with yields close to quantitative [9, 11, 17]. Treatment of benzo[*b*]tellurophene **1** with methyl bromide leads to the telluronium salt **24** [9]. Electrophilic substitution reactions, typical of benzannelated five-membered heterocycles, are complicated in the case of compound **1** by the ability of the dicoordinated tellurium atom to change to the tetracoordinated state and form complexes with various Lewis acids. Thus, 2-acetylbenzo[*b*]tellurophene was obtained with a yield of 10% during treatment of the benzotellurophene **1** with acetic anhydride in the presence of TiCl_4 [13]. If TiCl_4 is replaced by trifluoroacetic acid a mixture (76:24) of 2- and 3-acetylbenzo[*b*]tellurophenes is formed. The 2-acetyl-3-methyl-, 2-acetyl-3-bromo-, and 3-acetyl-2-methylbenzo[*b*]tellurophenes were synthesized from 3-methyl-, 3-bromo-, and 2-methyl-substituted derivatives of compound **1** under the same conditions with yields of 80, 40, and 25% respectively [13]. The treatment of benzotellurophene **1** with hexamethylenetetramine in the presence of trifluoroacetic acid gave its 2-formyl derivative with a yield of 10% [13].

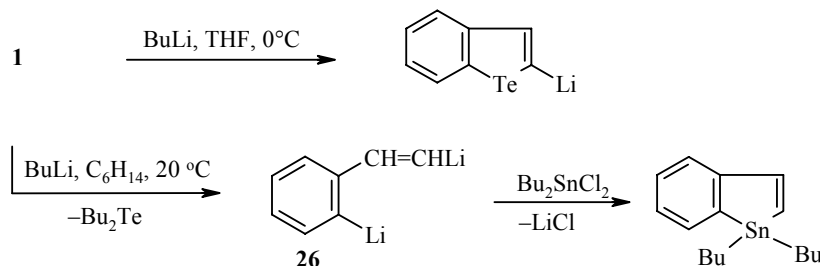
In contrast to benzo[*b*]thiophene, where halogenation takes place at positions 2 and 3 of the heterocycle, in the case of benzo[*b*]tellurophene **1** and also of its 3-substituted and 3,6-disubstituted derivatives the process takes place at position 2. Its first stage is the formation of σ -telluranes of type **23**. When compounds **23** (with $\text{R}^1 = \text{H}$) are boiled with halogens or SO_2Cl_2 in *o*-dichlorobenzene, 1,1,2-trihalobenzo[*b*]tellurophenes **25** are formed with yields of 50-80%. Reduction of the latter with hydrazine hydrate gave 2-halobenzo[*b*]tellurophenes.

The 1,1,2-tribromide **25** does not undergo further bromination. However, the bromination of 1,1,3-tribromobenzo[*b*]tellurophene gave 1,1,2,3-tetrabromobenzo[*b*]tellurophene, which was reduced by the action of hydrazine hydrate to the 2,3-dibromo derivative [13].

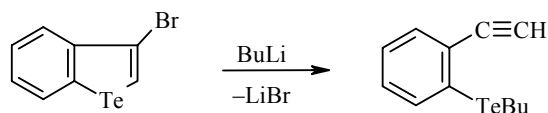


23 $\text{R}^1 = \text{COCl}$, $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{X} = \text{Cl}$; $\text{R}^1 = \text{COOH}$, $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{X} = \text{Br}$ [11]; **23**, **25** $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{X} = \text{Cl}$, Br [9]; $\text{R}^2 = \text{Cl}$, Br , $\text{R}^3 = \text{H}$, $\text{X} = \text{Cl}$ [17]; $\text{R}^2 = \text{Cl}$, $\text{R}^3 = \text{Me}$, Br , $\text{X} = \text{Cl}$ [1]

2-Lithiobenzo[*b*]tellurophene was obtained by the reaction of compound (**1**) with butyllithium (THF, 0°C) [11, 27]. Its carbonization led to benzo[*b*]tellurophene-2-carboxylic acid [11], reaction with DMF led to 2-formylbenzo[*b*]tellurophene (yield 60%), and reaction with methyl iodide and D_2O led to 2-methylbenzo[*b*]tellurophene (yield 88%) and 2-deuterobenzo[*b*]tellurophene (yield 98%) respectively [27]. If the reaction with butyllithium is conducted in hexane at 20°C , the C–Te bonds are cleaved with the formation of Bu_2Te and the dilithium derivative **26** [27]. Treatment of compound **26** with Bu_2SnCl_2 gave 1,1-dibutylbenzostannole with an 80% yield [27].



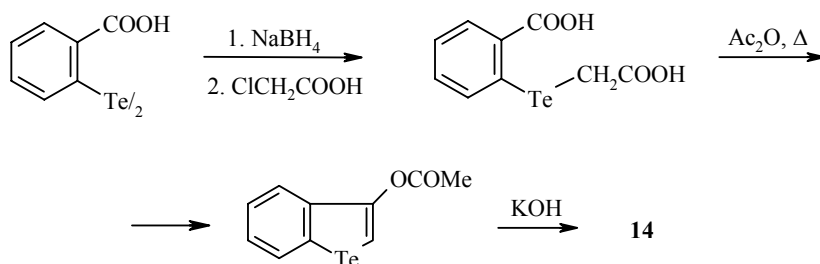
Attempts at the synthesis of 3-lithiobenzo[*b*]tellurophene by double decomposition of 3-bromobenzo[*b*]tellurophene with butyllithium were unsuccessful. Even at low temperatures the only product was 2-butyltellurophenylacetylene [17, 18].



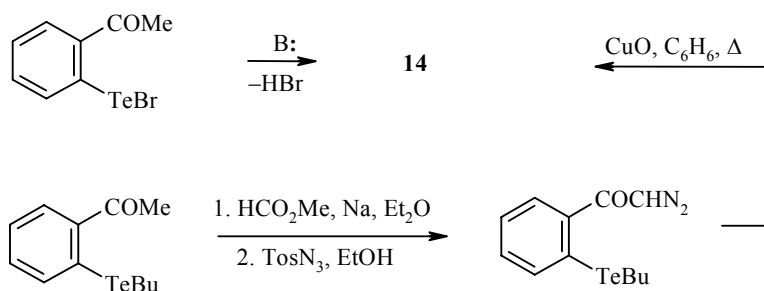
Benzo[*b*]tellurophenes containing the substituents COOH, COCl, CHO, COMe, and CN enter into the usual reactions for these groups [11, 13], and this made it possible to synthesize new representatives of the series.

1.3. 3-Oxo-2,3-dihydrobenzo[*b*]tellurophene and Its Derivatives

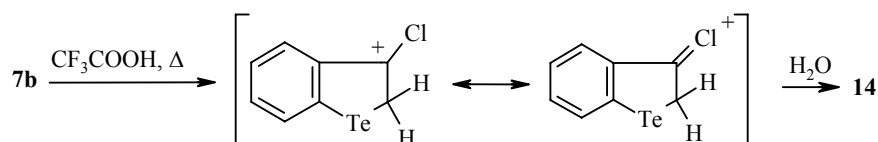
Telluroindoxyl **14** was first obtained by Renson [21] with a fairly low yield starting from (2-carboxyphenyl)telluroacetic acid.



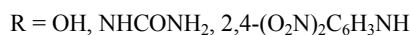
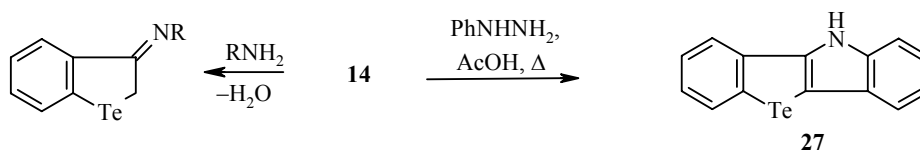
A preparative method for the production of compound **14** with a yield of 80% involves reaction of an alcohol solution of potassium hydroxide with 2-(bromotellurenyl)acetophenone [21]. Ammonia [28] or potassium acetate [29] can be used in place of potassium hydroxide. Another approach to the synthesis of the telluroindoxyl **14** (with a yield of 36%) was based on the intramolecular cyclization of 2-butyltellurodiazoacetophenone [30].



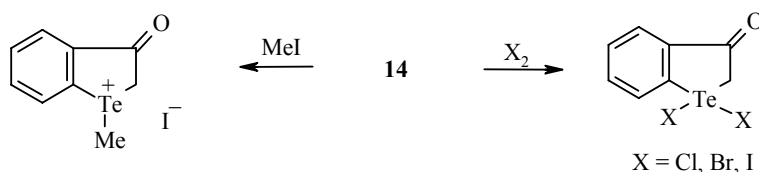
Compound **14** was obtained with a yield of 84% by boiling a solution of 3-chlorobenzo[*b*]tellurophene **7b** in trifluoroacetic acid [17]. It should be noted that 3-bromobenzo[*b*]tellurophene **7c** does not enter into such a reaction.



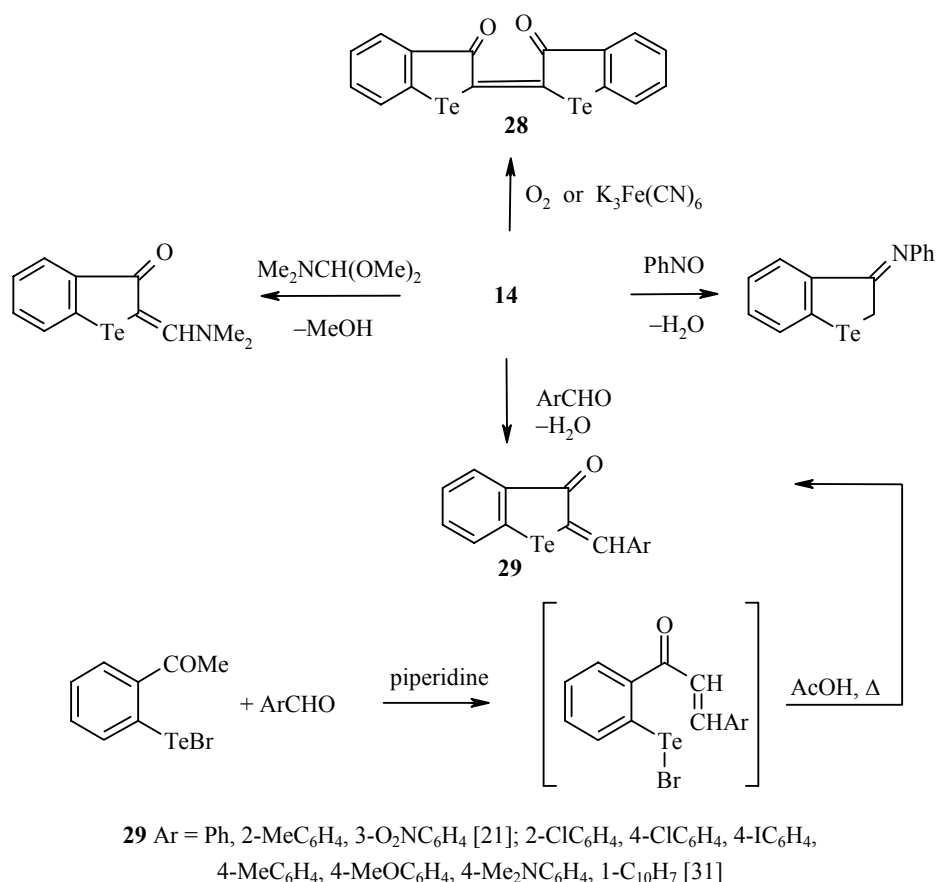
The telluroindoxyl **14** exists exclusively in the keto form in all solvents and does not form a 3-methoxy derivative when treated with dimethyl sulfate or methyl iodide in an alkaline medium. It enters readily into reactions characteristic of ketones, forming an oxime, a semicarbazone, and a 2,4-dinitrophenylhydrazone [21]. If it is boiled with phenylhydrazine in acetic acid, the tetracyclic product **27** is formed [21].



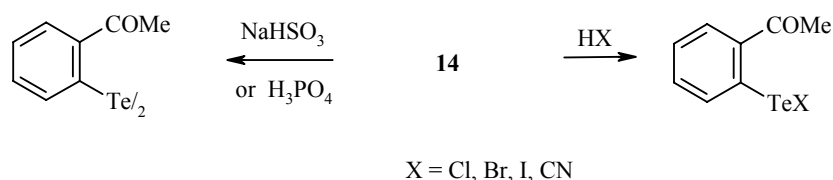
Like other derivatives of dicoordinated tellurium, compound **14** is oxidized by halogens to the corresponding σ -telluranes, while in reaction with methyl iodide it forms a telluronium salt [21].



When a solution of telluroindoxyl in DMF is heated for a long time [21] or during oxidation with K₃Fe(CN)₆ in an alkaline medium [29] telluroindigo **28** is formed as a violet crystalline compound with $\lambda = 637$ nm (for selenoindigo $\lambda = 564$ nm). Telluroindoxyl condenses readily with nitrosobenzene and DMF dimethyl acetal [21]. In reaction with aromatic aldehydes it forms 2-arylidene-3-oxo-2,3-dihydrobenzo[*b*]tellurophenes (telluroaurones) **29** [21]. These same compounds were obtained with yields of >80% by the condensation of 2-bromotellurenylacetophenone with aromatic aldehydes in the presence of piperidine [31]



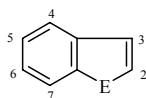
Telluroindoxyl is unstable in an acidic medium. During the action of acids under mild conditions the $\text{CH}_2\text{-Te}$ bond is cleaved, leading to 2-acetylphenyltellurenyl halides or tellurocyanate [21]. Reducing agents (NaHSO_3 and H_3PO_2) transform telluroindoxyl into bis(2-acetyl) ditelluride [32].



1.4. Physicochemical Characteristics of Benzo[*b*]tellurophene and Its Derivatives

For benzo[*b*]tellurophene **1** and its derivatives the photoelectronic [33], mass [34], and IR [35] spectra and also the ^1H [36, 37] and ^{125}Te [38, 39] NMR spectra have been investigated. As follows from analysis of the photoelectronic spectrum, the HOMO of compound **1** is mainly localized at the heteroatom, and this explains its ability to enter into oxidative addition. Table 1 presents data from the ^1H NMR spectra of benzo[*b*]tellurophene, benzo[*b*]furan, benzo[*b*]thiophene, and benzo[*b*]selenophene. It was shown that the chemical shifts of the protons at position 3 correlate with the electronegativity of the heteroatom [36, 40, 41].

TABLE 1. The ^1H NMR Spectra of Benzofuran, Benzothiophene, and Benzotellurophene



| Position of protons | Chemical shifts, δ , ppm. | | | | J | SSCC, J , Hz | | | |
|---------------------|----------------------------------|----------|-----------|-----------|-----------|----------------|----------|-----------|-----------|
| | E=O [40] | E=S [41] | E=Se [37] | E=Te [37] | | E=O [40] | E=S [41] | E=Se [37] | E=Te [37] |
| 2 | 7.52 | 7.27 | 7.79 | 8.55 | $J_{2,3}$ | 2.19 | 5.57 | 5.57 | 6.95 |
| 3 | 6.66 | 7.19 | 7.42 | 7.84 | $J_{3,5}$ | 0.87 | 0.86 | 0.65 | 0.43 |
| 4 | 7.49 | 7.70 | 7.69 | 7.71 | $J_{4,5}$ | 7.89 | 8.09 | 7.97 | 7.97 |
| 5 | 7.13 | 7.25 | 7.24 | 7.26 | $J_{4,6}$ | 1.28 | 1.16 | 1.02 | 1.07 |
| 6 | 7.19 | 7.22 | 7.14 | 7.03 | $J_{4,7}$ | 0.80 | 0.73 | 0.48 | 0.51 |
| 7 | 7.42 | 7.77 | 7.77 | 7.82 | $J_{5,6}$ | 7.27 | 7.22 | 7.22 | 7.24 |
| | | | | | $J_{5,7}$ | 0.92 | 1.17 | 1.17 | 1.08 |
| | | | | | $J_{6,7}$ | 8.43 | 8.06 | 8.27 | 8.00 |

The ^{125}Te chemical shifts of a series of monosubstituted benzotellurophenes are given in [38, 39]. They are more sensitive to the nature of the substituents than the ^{77}Se chemical shifts in the corresponding benzo[*b*]selenophenes. A good linear correlation was obtained between the ^{125}Te chemical shifts of benzo[*b*]tellurophenes and of tellurophenes containing the same substituents, which demonstrates the similarity in the mechanism of transmission of the electronic effects of the latter in both heterocycles.

The ionization constants ($\text{p}K_a$) of benzo[*b*]tellurophene-2-carboxylic acid and its hetero analogs are given in Table 2. In the transition from benzofuran-2-carboxylic acid to benzo[*b*]tellurophene-2-carboxylic acid the $\text{p}K_a$ value increases by approximately 1.0 [42]. Comparison of these $\text{p}K_a$ values with the $\text{p}K_a$ values of

TABLE 2. The Ionization Constants ($\text{p}K_a$)* and ν_{CO} Values of the Hetero

Analogs [42]. The Solvolysis Characteristics (30% EtOH,

60°C) of the Hetero Analogs [43]

| E | $\text{p}K_a$ | ν_{CO}^{*2} | $k \cdot 10^3 \cdot \text{s}^{-1}$ | k_E/k_S^{*3} | $k_B/k_M \cdot 10^3 \cdot \text{s}^{-1}$ |
|----|---------------|------------------------|------------------------------------|----------------|--|
| O | 4.20 (4.54) | 1758 (1755) | 0.95 | 1.5 | 4.8 |
| S | 4.67 (5.05) | 1733 (1734) | 0.63 | 1.0 | 9.7 |
| Se | 4.79 (5.14) | 1731 (1728) | 1.04 | 1.7 | 9.5 |
| Te | 5.13 (5.48) | 1716 (1721) | 3.26 | 5.2 | 8.9 |

* The $\text{p}K_a$ value was determined by potentiometry in a 1:1 mixture of water and ethanol [42]; the $\text{p}K_a$ values of the corresponding nonannelated hetero analogs are given in parentheses.

*² The ν_{CO} values of the nonannelated heterocycles are given in parentheses [42].

*³ k_E is the solvolysis rate constant of the respective heterocycle, k_S is the solvolysis rate constant of 1-(2-benzo[*b*]thienyl)ethyl acetate [43].

*⁴ k_B is the solvolysis rate constant of the benzannelated derivatives, k_M is the same for the monocyclic derivatives [43].

tellurophene-2-carboxylic acid and its hetero analogs [42] shows that benzannelation reduces the pK_a value by approximately 0.35 irrespective of the nature of the heteroatom. It should be noted that in contrast to the 2-carboxy derivatives the pK_a values of benzo[*b*]tellurophene-3-carboxylic acid and its benzo[*b*]furan, benzo[*b*]thiophene, and benzo[*b*]selenophene analogs are close to each other (5.79, 5.54, 5.67, and 5.65 respectively) [13].

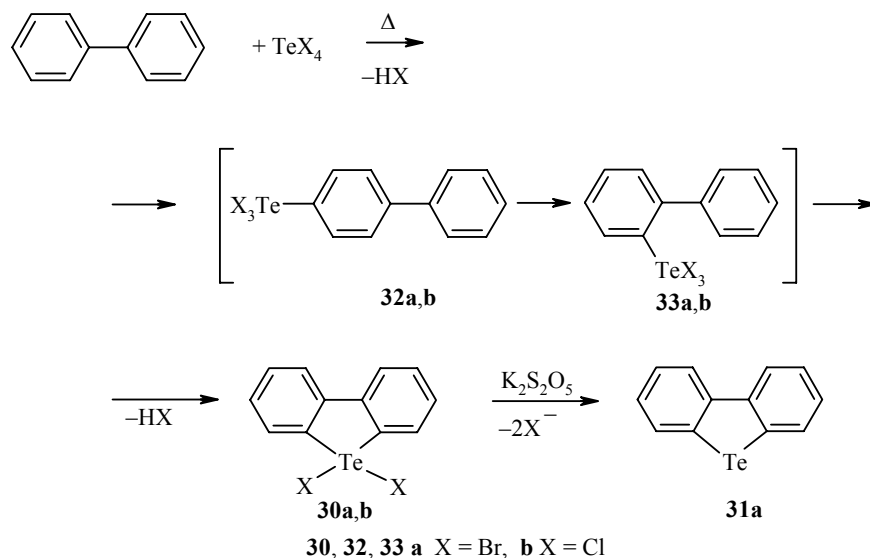
Table 2 also gives data on the kinetics of the solvolysis of 1-(2-hetaryl)ethyl acetates [43], which show that the solvolysis rate decreases in the series of derivatives in the following order: Benzotellurophene > benzoselenophene > benzofuran > benzothiophene.

2. DIBENZO[*b,d*]TELLUROPHENE

Some data on dibenzo[*b,d*]tellurophene and its derivatives, published after 1985, were reviewed in [4-6].

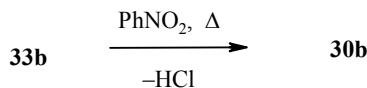
2.1. Synthesis of Dibenzo[*b,d*]tellurophene and Its Derivatives

The first representative of dibenzotellurophenes, 5,5-dibromobenzotellurophene (**30a**), was obtained with a low yield by the reaction of biphenyl with TeBr_4 at 240-250°C [3]. Reaction with TeCl_4 leads to the 5,5-dichloride **30b** with a higher yield. Both dihalides are easily reduced to dibenzotellurophene **31a** by the action of $\text{K}_2\text{S}_2\text{O}_5$ [3]. A possible mechanism for the production of the dihalides **30** involves the initial formation of 4-biphenyltellurium trihalides **32** and their rearrangement to the 2-isomers **33**, which undergo cyclization with the elimination of HX (X = Cl, Br). A similar mechanism was proposed for the reaction of diphenyl ether with TeCl_4 , leading to 10,10-dichlorophenoxatellurin [44].

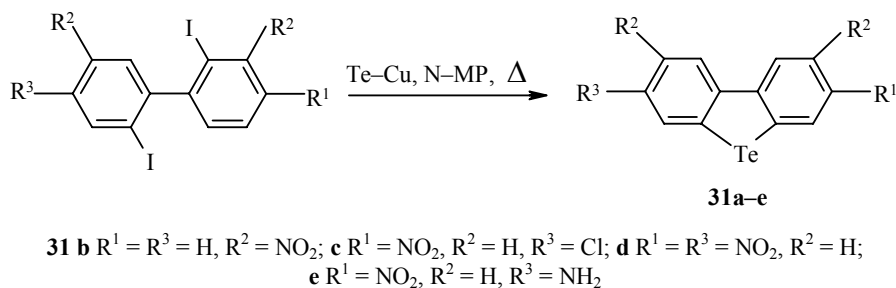


If the reaction between biphenyl and TeCl_4 is carried out at a lower temperature (140-160°C), it stops at the formation of the trichloride **32b** and does not lead to the product **30b**, as stated in [45]. In fact, reduction of the reaction product with sodium sulfide gives red-orange crystals melting at 175.5°C [clearly, bis(2-biphenyl) ditelluride], whereas the dibenzotellurophene **31a** is a light-yellow compound with a melting point of 92.0-94.5°C.

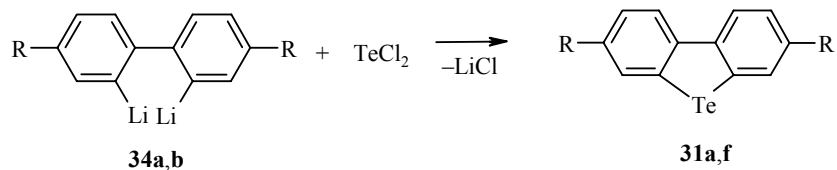
The 5,5-dichloride **30b** was obtained with an almost quantitative yield by boiling 2-diphenyltellurium trichloride **33b** (synthesized from biphenylmercury chloride and TeCl₄ with a yield of 76% or from 2-lithiobiphenyl and TeCl₄ with a yield of 16%) in nitrobenzene [46].



It is clear that the most general method for the synthesis of dibenzotellurophenes is the reaction of 2,2'-diiodobiphenyls with a "tellurizing" agent in N-methylpyrrolidone (N-MP) [47]. This agent, denoted as Te-Cu, is produced by the reaction of Na₂Te with CuI (ratio 1:2) in N-MP. Its structure was not determined precisely; it was assumed that it was a mixture of Te-containing compounds, elemental tellurium, and metallic copper [47]. The yields of the dibenzotellurophenes **31a-e** amounted to 40-52%.

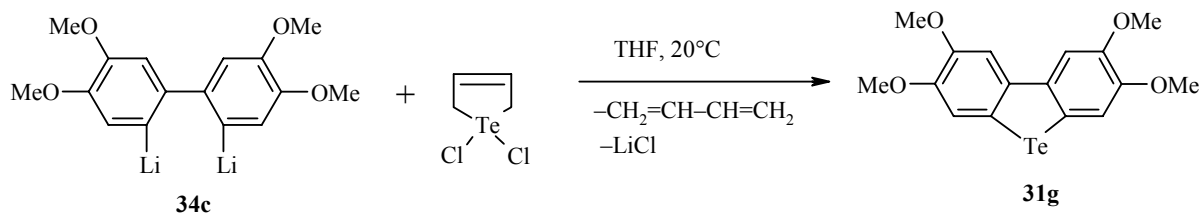


In other methods for the synthesis of compounds of type **31** 2,2'-dilithiobiphenyls and mercuriobiphenyls were used as starting compounds [48-51]. Thus, dibenzotellurophenes **31a,f** were obtained with yields of 52-54% in the reaction of the dilithium derivatives **34a,b** with TeCl₂ [48, 49, 51]. If the synthetic equivalent 1,1-dichloro-2,5-dihydrotellurophene was used in place of TeCl₂ [52] the yield of the heterocycle **30a** was increased to 78% [53].

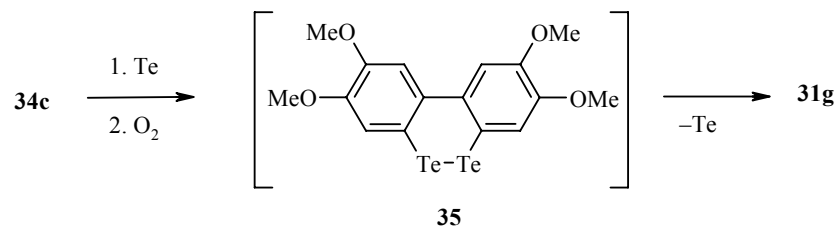


31 f, **34 b** R = Me; **34 a** R = H

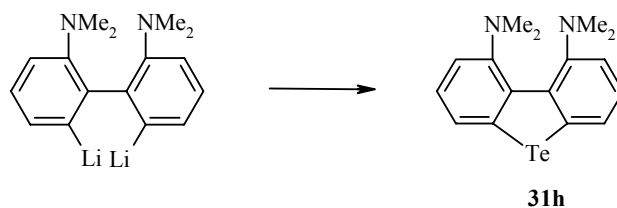
However, in the reaction of the dilithium derivative **34c** with 1,1-dichloro-2,5-dihydrotellurophene the product **31g** was obtained with a yield of 13% [53].



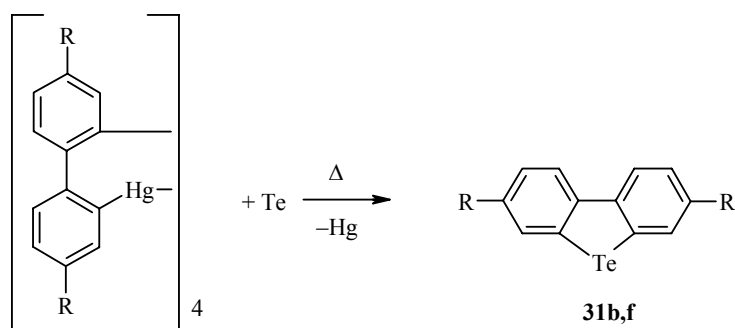
By analogy with the reactions of aryllithiums with tellurium, which leads after oxidation of the formed lithium tellurophenolates ArTeLi to diaryl tellurides, it could be expected that treatment of the dilithium derivative **34c** with tellurium followed by oxidation with atmospheric oxygen would lead to the product **35** with a six-membered ring containing two Te atoms. However, the only reaction product is the dibenzotellurophene **31g**, which is probably formed by elimination of the tellurium atom from compound **35**.



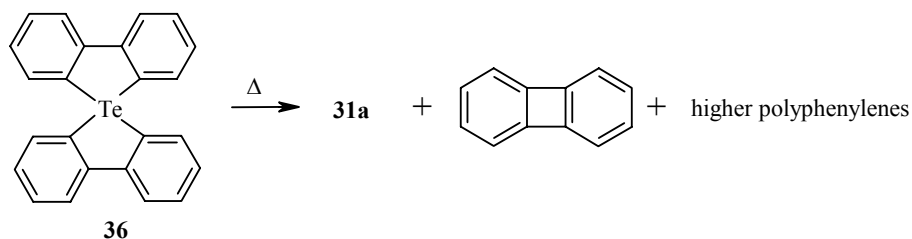
It should be noted that the selenium analog of the latter was isolated with a yield of only 4% [53] and the yield of the dibenzotellurophene **31h** was extremely low [54].



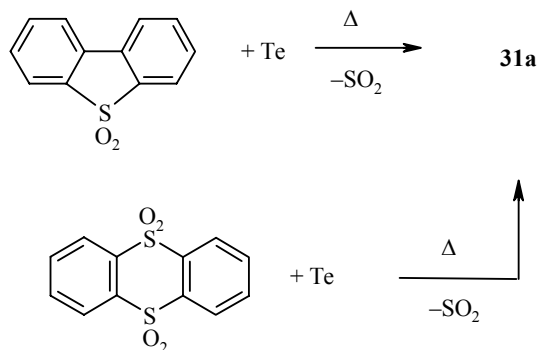
The dibenzotellurophenes **31b,f** were obtained with fairly high yields (79-82%) by heating tellurium with the tetrameric 2-mercurio-2,2'-biphenylenes [48, 49, 51]. However, the poor accessibility of the latter makes this reaction unsuitable for preparation of the products.



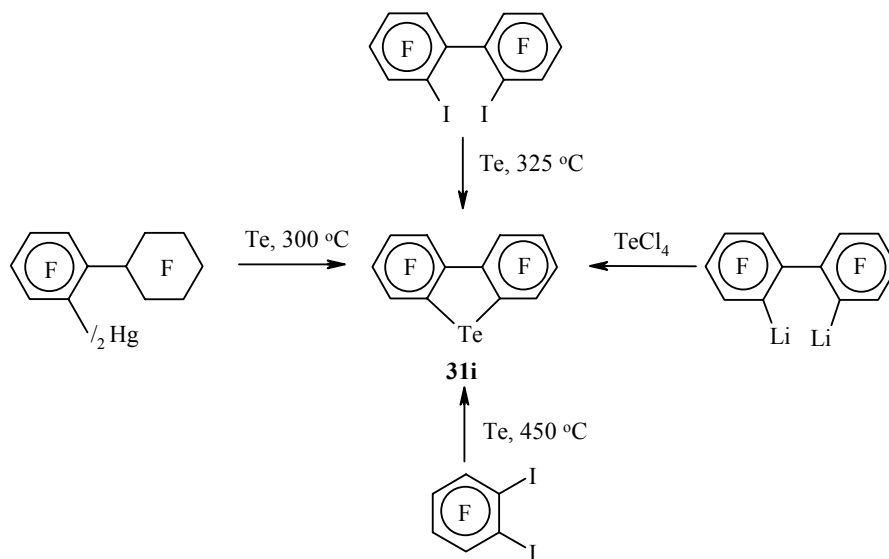
The same can be said of the production of the dibenzotellurophene **31a** by thermal decomposition of bis(2,2'-biphenylene)tellurium **36** [48, 49, 51, 55]. Since the precursor of the spiran **36** is 2,2'-dilithiobiphenyl, which can be converted directly into compound **31a**, this reaction does not have significant synthetic value.



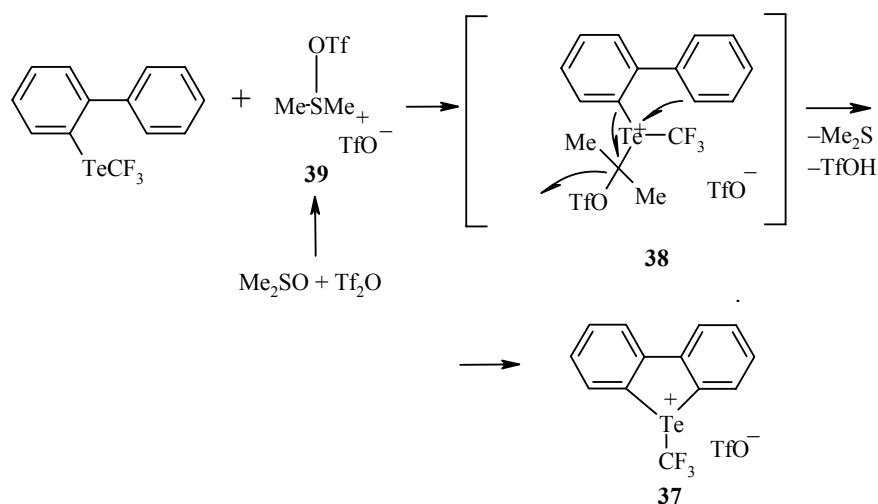
A specific method for the synthesis of the dibenzotellurophene **31a**, which can clearly be used for the production of other tellurium-containing heterocycles, involves heating dibenzothiophene S,S-dioxide with powdered tellurium [56]. However, the yield of the product **31a** was only 10%. Compound **31a** was also obtained with a small yield by heating 5,5,10,10-thianthrene tetroxide with amorphous tellurium [57].



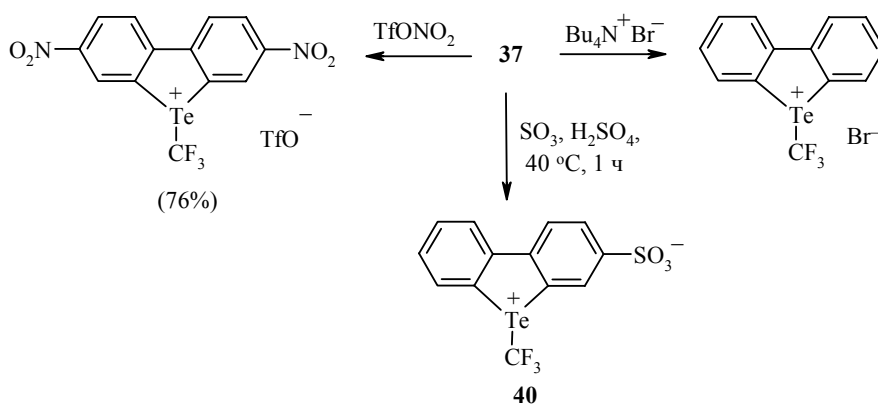
The synthesis of octafluorodibenzotellurophene **31i** was realized by the high-temperature reaction of tellurium with 2,2-diiodooctafluorobiphenyl (yield 66%) [58], 1,2-diiodotetrafluorobenzene (yield 17%) [59, 60], and bis(2-nonafluorobiphenyl)mercury (yield 10%) [59]. The same product was obtained with a yield of 17% from 2,2'-dilithiooctafluorobiphenyl and TeCl_4 [58]. It should be noted that the corresponding dibenzotellurophene 5,5-dichlorides are formed in the reaction of 2,2'-dilithiobiphenyls **34a** [48, 49] and **34c** [53] with TeCl_4 .



Te-(Trifluoromethyl)dibenzotellurophenium triflate **37** was obtained with a yield of 84% by the reaction of 2-biphenyl trifluoromethyl telluride with DMSO and Te_2O [61, 62]. The intermediate in this reaction is probably the salt **38**, formed by attack of the sulfonium salt **39** at the tellurium atom.



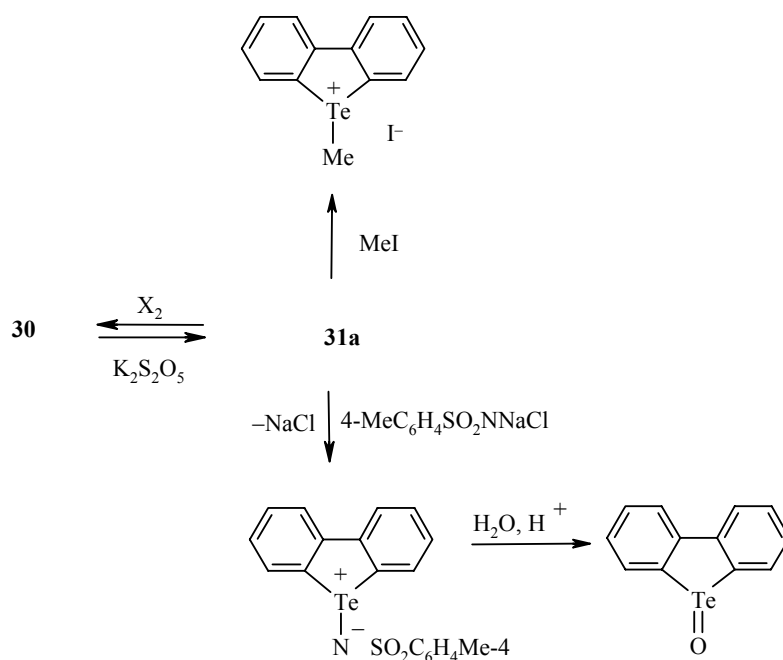
The salt **37** was also obtained from 2-biphenyl trifluoromethyl telluride and bromine in methylene chloride followed by the addition of TfOH to the reaction mixture [62]. Some reactions of the salt **37** [62, 63] are shown below.



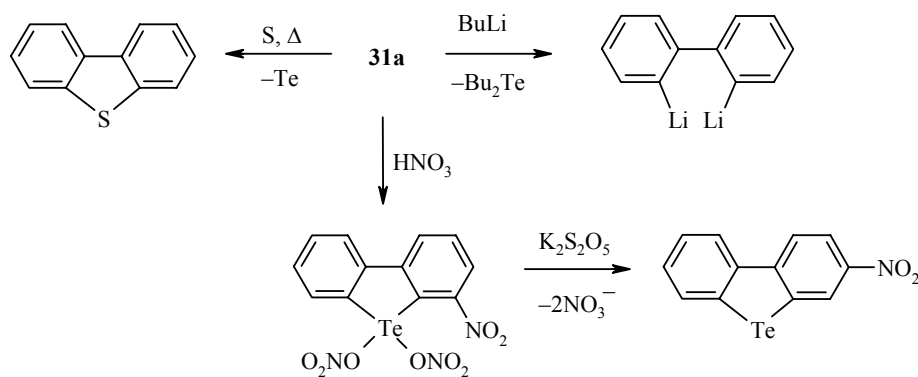
The salt **37** and its sulfur and selenium analogs are electrophilic trifluoromethylating compounds, the reactivity of which increases in the order $\text{Te} < \text{Se} < \text{S}$ [62]. From the practical stand point it is more convenient to use salts of type **40** [63], since they have strong trifluoromethylating ability, while the side products of the reaction – dibenzotellurophene-3-sulfonic acid and its analogs – are soluble in water and are easily separated from the trifluoromethylation products.

2.2. Reactions of Dibenzo[*b,d*]tellurophene and Its Derivatives

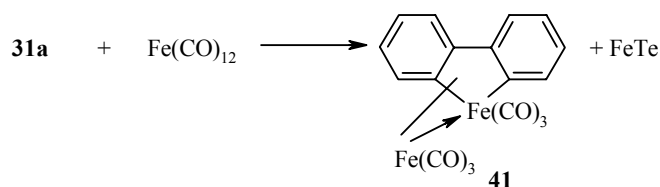
Like other tellurium-containing compounds, dibenzo[*b,d*]tellurophene **31a** enters readily into oxidative addition of halogens, forming dibenzotellurophene 5,5-dihalides with high yields [46, 48, 49]. Since the latter are easily reduced to the initial compound by the action of $\text{K}_2\text{S}_2\text{O}_5$, the transformations are used for the purification of dibenzotellurophene [48, 49]. Reaction with methyl iodide leads to Te-methyldibenzotellurophenium iodide, which is unstable and decomposes when heated in ethanol. Treatment of dibenzo[*b,d*]tellurophene with chloramine-T gave 2,2'-biphenylenetelluriosylamine [49, 51]. Hydrolysis of this compound leads to dibenzotellurophene oxide [49]. Synthesis of the latter was also achieved by hydrolysis of dibenzotellurophene 5,5-dichloride [3].



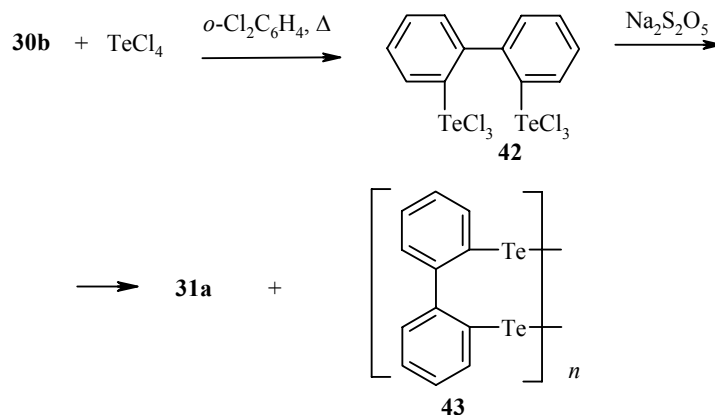
Treatment of dibenzotellurophene **31a** with an excess of butyllithium led to cleavage of both C–Te bonds, resulting in the formation of 2,2'-dilithiobiphenyl and dibutyl telluride [50]. When compound **31a** is heated with powdered sulfur the tellurium atom is substituted by a sulfur atom [3]. The action of concentrated nitric acid leads to 3-nitrodibenzotellurophene 5,5-dinitrate, which on reduction gives 3-nitrobenzotellurophene [57].



Dibenzotellurophene forms stable 1:1 adducts with HgCl_2 , 1,3,5-trinitrobenzene [49], picric acid [49, 64], and tetracyanoquinodimethane (TCQDM) [65]. It is detellurized by triiron dodecacarbonyl, where the main products are the dibenzoferrule **41**, isolated with a yield of 28%, and FeTe [66].



Like the noncyclic diaryltellurium dichlorides, which form aryltellurium trichlorides in reaction with TeCl_4 [67], the dibenzotellurophene 5,5-dichloride **30b** is converted into 2,2-bis(trichlorotelluro)biphenyl **42** (yield 87%) when boiled with TeCl_4 in *o*-dichlorobenzene [68]. Reduction of this product with an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_5$ gives the poly(*o*-phenyleneditelluride) **43**, contaminated with metallic tellurium impurity; a side product of the reaction is dibenzotellurophene **31a**, isolated with a yield of 8%.



2.3. Molecular and Crystal Structure of Dibenzotellurophene and Its Derivatives*

The molecular and crystal structures of dibenzotellurophene **31a** [69], its complex with TCQDM [65], and dibenzotellurophene 5,5-diiodide [70] were studied by X-ray crystallographic analysis. The dibenzotellurophene molecule is practically planar; the dihedral angles between the benzene rings and the heterocycle amount to 1.4 and 0.6°. The length of the Te–C bond (2.087 Å) is within the normal limits for such bonds [71]. The C–Te–C bond angle (81.7°) is the smallest in the series of related heterocyclic systems containing elements of group VIA as heteroatoms.

Dibenzotellurophene 5,5-diiodide has the structure of a trigonal bipyramid [70]. The dibenzotellurophene fragment of this compound shows a greater departure from planarity compared with dibenzotellurophene: The dihedral angles are 3.3°. The Te–C bond length (2.12 Å) and the C–Te–C bond angle (81.8°) are almost the same as in dibenzotellurophene. The iodine atoms occupy the apical positions. The Te–I bond length is 2.936 Å, and the I–Te–I angle is 178.5°. The Te atom forms weak intermolecular bonds with the I atoms of two neighboring molecules; the $\text{Te}\cdots\text{I}$ bond lengths are 3.717 and 3.696 Å. (The sum of van der Waals radii of Te and I is 4.35 Å [72].) Thus, with allowance for the secondary bonds the coordination polyhedron at the Te atom represents an octahedron. The $\text{Te}\cdots\text{I}$ interactions link the individual molecules of the diiodide in the crystal into polymeric chains.

In the ^{125}Te NMR spectrum the chemical shift for dibenzotellurophene amounts to 486.3 ppm [73]. The mass spectra of octafluorodibenzotellurophene were studied in [74].

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* See also: E. Lukevics, P. Arsenyan, S. Belyakov, and O. Pudova, *Khim. Geterotsykl. Soedin.*, 867 (2002) or *Chem. Heterocyclic Compds*, 763 (2002). Editor's comment.

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