Five-, six- and eight-membered tellurium-containing heterocycles with vicinal Te, O and Te, N heteroatoms

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Dedicated to Academician Mikhail G. Voronkov in recognition of his outstanding contribution to diverse areas of organic and organoelement chemistry and on the occasion of his 80th birthday
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Abstract
Previously undescribed tellurium-containing heterocycles (5H-oxatelluroles-1,2 and their benzoderivatives, 1,2,3-telluradiazines and 1,2,6-oxatellurazocines) were prepared by dehydrohalogenation of the aromatic or alkene compounds containing vicinal Te(R)Hal₂ or TeHal and hydroxy or NH groups. The same procedure was used for the synthesis of isotellurazoles. By oxidation of β-aryltelluroallylic alcohols and o-aryltellurobenzoic acids 5H-1,2-oxatelluroles and 3H-2,1-benzoatelluroyl-3-ones have been prepared in good yields.

Keywords: 1-Aryl-1-chloro-2,1-benzoatelluroyl-3-ones, N-arylisotellurazolium perchlorates, 2-aryl-1,2,3-telluradiazines, 7,8-benzo-1,2,6-oxatellurazocines, 3H-2,1-benzoatelluroles, dehydrohalogenation, isotellurazoles, 5H-oxatelluroles-1,2, oxidation, spiro[3H-2,1-benzoatellurole], tellurium-containing heterocycles

Introduction
Derivatives of 1,2-telluroles represent the most thoroughly studied group of five-membered tellurium-containing heterocycles with two vicinal heteroatoms.¹ The interest in these compounds has been mostly because of their use as the donor components of conducting charge-transfer complexes and radical-ion salts. The heterocyclic compounds with Te, O centers in the positions 1,2 of a five-membered ring have been first described in our papers. Of Te, N-containing heterocycles of this type only benzisotellurazole² was known at the beginning of our work and some of the 3-substituted and 3,5-disubstituted isotellurazoles³ had been prepared in
very low yields. This paper gives a brief survey of our study in the area and contains also some recently obtained results.

The principal method employed for the synthesis of 1,2-Te,O- and 1,2-Te,N-heterocycles consists in dehydrohalogenation of the arene or vinylene compounds containing vicinal Te(R)Hal₂ or TeHal and OH or NHR groups. This approach has been used for the synthesis of 5H-1,2-oxatelluroles and their benzo analogues 1, isotellurazoles 2, 1,2,3-telluradiazines 3 and 1,2,6-oxatellurazocines 4.

The synthesis of 5H-1,2-oxatelluroles 1 and 1,2-oxatellurol-5-ones 5 and their dihydro derivatives 6 has been performed by oxidation of 3-(aryltelluro)propen-2-ols-3 and 2-aryltellurobenzoic and β-aryltelluropropionic acids with tert-butyl hypochlorite.

β-Organyltellurovinylaldehydes and ketones as well as their imines serve as useful synthons for the preparation of heterocycles 1-4. The synthesis, reactions, spectral and structural characterization of these compounds are described elsewhere 4-8.

1. 5H-1,2-Oxatelluroles and their benzo analogues
3-(Aryltelluro)propen-2-ols 8 and 2-butyltellurobenzylic alcohols 9 serves as precursors of 5H-oxatelluroles-1,2, 1 and their benzoanalogues 7 (I, R₁ + R₂ = (CH=CH)₂). The synthesis of compounds 8, which are obtained exclusively in Z-isomeric forms, and 9 has been previously described in much detail. 9-13 Two different methods have been applied for the cyclization of the alcohols 8,9 into the heterocycles 1, 7. The first one applied mostly for the synthesis of 2-aryl-2-chloro-5H-oxatelluroles-1,2 1 consists in the oxidation of 8 with tert-butylhypochlorite. 9-10 The reaction affords the heterocycles 1 in 44-82% yield and involves σ–telluranes 10 as the
intermediates. The compounds 1a-g thus obtained and also 2-aryl-2-ido-5H-oxatelluroles 1h,i prepared by the halogen exchange reaction from 1d,f are characterized in Table 1.

![Chemical structures](image)

**Table 1. Characteristics of 1,2-Oxatelluroles 1a-i**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular formula</th>
<th>Mp (°C)</th>
<th>$^1$H NMR, δ, ppm</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>C$<em>{15}$H$</em>{13}$ClOTe</td>
<td>115</td>
<td>2.13 (8H, m, 4CH$_2$), 4.90 (2H, dd, $J = 17.0$ Hz, 3-H), 7.63 (5H, m, C$_6$H$_5$)</td>
<td>79</td>
</tr>
<tr>
<td>1b</td>
<td>C$<em>{13}$H$</em>{15}$ClOTe</td>
<td>118.5</td>
<td>6.02 and 6.26 (1H, s, s, 3α or β-H), 7.45 (12H, m, 2C$_6$H$_5$ + CH=CH)</td>
<td>82</td>
</tr>
<tr>
<td>1c</td>
<td>C$<em>{15}$H$</em>{13}$ClOTe</td>
<td>126</td>
<td>5.27 (2H, dd, $J = 17.8$ Hz, CH$_2$), 7.54 (7H, m, C$_6$H$_5$ + CH=CH)</td>
<td>44</td>
</tr>
<tr>
<td>1d</td>
<td>C$_9$H$_9$ClOTe</td>
<td>128</td>
<td>5.15 (2H, dd, $J = 18.0$ Hz, 3-H), 7.44 (10H, m, C$_6$H$_5$ + C$_6$H$_4$ + 4-H)</td>
<td>75</td>
</tr>
<tr>
<td>1e</td>
<td>C$<em>{17}$H$</em>{17}$ClO$_2$Te</td>
<td>130.5</td>
<td>1.40 (3H, t, CH$_3$), 4.05 (2H, q, OCH$_2$), 5.18 (2H, dd, $J = 18.1$ Hz, 3-H), 7.32 (2H, m, CH=CH), 8.12 (2H, d, 2′-, 6′-H)</td>
<td>45</td>
</tr>
<tr>
<td>1f</td>
<td>C$<em>{11}$H$</em>{13}$ClO$_2$Te</td>
<td>115</td>
<td>5.15 (2H, dd, $J = 18.0$ Hz, 3-H), 6.96 (2H, d, 3′-,5′-H), 7.32 (2H, m, CH=CH), 8.12 (2H, d, 2′-, 6′-H)</td>
<td>47</td>
</tr>
<tr>
<td>1g</td>
<td>C$<em>{10}$H$</em>{11}$ClO$_2$Te</td>
<td>118</td>
<td>3.81 (3H, s, OCH$_3$), 5.17 (2H, dd, $J = 18.1$ Hz, 3-H), 6.97 (2H, d, 3′-,5′-H), 7.30 (2H, m, CH=CH), 7.82 (2H, d, 2′-, 6′-H)</td>
<td>82</td>
</tr>
<tr>
<td>1h</td>
<td>C$_9$H$_9$IOTe</td>
<td>120</td>
<td>5.15 (2H, dd, $J = 18.0$ Hz, CH$_2$), 7.59 (7H, m, C$_6$H$_5$ + CH=CH)</td>
<td>84</td>
</tr>
<tr>
<td>1i</td>
<td>C$<em>{11}$H$</em>{13}$IO$_2$Te</td>
<td>104</td>
<td>1.40 (3H, t, CH$_3$), 4.03 (2H, q, OCH$_2$), 5.25 (2H, dd, $J = 18.5$ Hz, 3-H), 7.37 (6H, m, C$_6$H$_4$ + CH=CH)</td>
<td>84</td>
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</tbody>
</table>
Dehydrohalogenation of primary and secondary 2-butyldihalogenotellurobenzylc alcohol 11 leads to 3\(H\)-2,1-benzoxatelluroles 7\(^{9,12,13}\). The advantage of this approach is a possibility of preparing benzoxatelluroles with various halogen atoms at the tellurium center. Conditions for the dehydrohalogenation of the alcohols 11 obtained in high yields by the oxidation-addition reaction of the tellurides 9 with dihalogens (Cl\(_2\), Br\(_2\), I\(_2\))\(^{9,12,13}\) crucially depends on the origin of the halogen atoms attached to the tellurium center. Thus, 2-butyldifluorotellurobenzylc alcohol (prepared by the halogen exchange reaction between 2-butyldibromotellurobenzylc alcohol and AgF) spontaneously forms 1-butyl-1-fluoro-2,1-benzoxatellurole 7\(d\) (87\%)\(^{9,12}\). The cyclization of 2-butyldihalogenotellurobenzylc alcohols 11 occurs on treatment with triethylamine \(^{9,12,13}\). Oxa-1 and benzoxatelluroles 7 with a substituent in the 3 position are obtained as mixtures of two diastereomers as determined by \(^1\)H NMR spectra \(^{9,12}\). Table 2 contains some data on the compounds 7.

\[
\begin{align*}
\text{a-d} & \quad R = H: \quad X = \text{Cl (a), Br (b), I (c), F (d); e-g} \quad R = \text{Ph: Cl (e), Br (f), I (g); h-j} \quad R = 4-\text{MeC}_6\text{H}_4: \quad X = \text{Cl (h), Br (i), I (j); k-m} \quad R = \text{Me: Cl (k), Br (l), I (m).}
\end{align*}
\]

Dehydrohalogenation of the alcohol 12 prepared from the corresponding telluride by the oxidation-addition reaction with chlorine \(^{14}\) gives rise to 1,1'-spiro[3\(H\)-2,1-benzoxatellurole] 13. The treatment of a benzene solution 12 with two equivalents of triethylamine affords 13 in almost quantitative yield. 3,3,3,3-Tetramethyl- and 3,3,3,3-tetra(trifluoromethyl)-1,1'-spiro[3\(H\)-
2,1-benzoxatelluroles] were also synthesized in 20-60% yields by coupling arylmagnesium chlorides containing $\text{o-CMe}_2\text{OMgBr}$ and $\text{C(CF}_3\text{)}_2\text{OMgBr}$ groups with tellurium tetrachloride $^{15}$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular formula</th>
<th>Mp (°C)</th>
<th>$^1\text{NMR}, \delta, \text{ppm}$</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>$\text{C}<em>{11}\text{H}</em>{15}\text{ClOTe}$</td>
<td>114-115</td>
<td>1.79 (9H, m, $\text{C}_4\text{H}_9$), 5.32 (2H, dd, $J = 15.3$ Hz, 3-H), 7.68 (4H, m, $\text{C}_6\text{H}_4$)</td>
<td>89</td>
</tr>
<tr>
<td>7b</td>
<td>$\text{C}<em>{11}\text{H}</em>{15}\text{BrOTe}$</td>
<td>113-114</td>
<td>1.96 (9H, m, $\text{C}_4\text{H}_9$), 5.41 (2H, dd, $J = 15.1$ Hz, 3-H), 7.80 (4H, m, $\text{C}_6\text{H}_4$)</td>
<td>78</td>
</tr>
<tr>
<td>7c</td>
<td>$\text{C}<em>{11}\text{H}</em>{15}\text{IOTe}$</td>
<td>110-112</td>
<td>2.19 (9H, m, $\text{C}_4\text{H}_9$), 5.37 (2H, dd, $J = 15.1$ Hz, 3-H), 7.72 (4H, m, $\text{C}_6\text{H}_4$)</td>
<td>75</td>
</tr>
<tr>
<td>7d</td>
<td>$\text{C}<em>{11}\text{H}</em>{15}\text{FOTe}$</td>
<td>Oil</td>
<td>1.83 (9H, m, $\text{C}_4\text{H}_9$), 5.45 (2H, dd, $J = 15.2$ Hz, 3-H), 7.80 (4H, m, $\text{C}_6\text{H}_4$)</td>
<td>87</td>
</tr>
<tr>
<td>7e</td>
<td>$\text{C}<em>{17}\text{H}</em>{19}\text{ClOTe}$</td>
<td>127-128</td>
<td>2.27 (9H, m, $\text{C}_4\text{H}_9$), 6.40 and 6.71 (1H, s, s, 3α or β-H), 7.91 (9H, m, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4$)</td>
<td>70</td>
</tr>
<tr>
<td>7f</td>
<td>$\text{C}<em>{17}\text{H}</em>{19}\text{BrOTe}$</td>
<td>138-139</td>
<td>2.11 (9H, m, $\text{C}_4\text{H}_9$), 6.28 and 6.57 (1H, s, s, 3α or β-H), 7.75 (9H, m, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4$)</td>
<td>82</td>
</tr>
<tr>
<td>7g</td>
<td>$\text{C}<em>{17}\text{H}</em>{19}\text{IOTe}$</td>
<td>140-142</td>
<td>1.99 (9H, m, $\text{C}_4\text{H}_9$), 6.17 and 6.42 (1H, s, s, 3α or β-H), 7.00 (9H, m, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4$)</td>
<td>76</td>
</tr>
<tr>
<td>7h</td>
<td>$\text{C}<em>{18}\text{H}</em>{21}\text{ClOTe}$</td>
<td>140-141</td>
<td>2.22 (9H, m, $\text{C}_4\text{H}_9$), 2.42 (3H, s, 4-CH$_3$), 6.38 and 6.78 (1H, s, s, 3α or β-H), 7.87 (8H, m, 2C$_6$H$_4$)</td>
<td>79</td>
</tr>
<tr>
<td>7i</td>
<td>$\text{C}<em>{18}\text{H}</em>{21}\text{BrOTe}$</td>
<td>138-140</td>
<td>2.05 (9H, m, $\text{C}_4\text{H}_9$), 2.33 (3H, s, 4-CH$_3$), 6.29 and 6.70 (1H, s, s, 3α or β-H), 7.78 (8H, m, 2C$_6$H$_4$)</td>
<td>84</td>
</tr>
<tr>
<td>7j</td>
<td>$\text{C}<em>{18}\text{H}</em>{21}\text{IOTe}$</td>
<td>100-102</td>
<td>1.98 (9H, m, $\text{C}_4\text{H}_9$), 2.26 (3H, s, 4-CH$_3$), 6.10 and 6.65 (1H, s, s, 3α or β-H), 7.60 (8H, m, 2C$_6$H$_4$)</td>
<td>62</td>
</tr>
<tr>
<td>7k</td>
<td>$\text{C}<em>{12}\text{H}</em>{17}\text{ClOTe}$</td>
<td>124-125</td>
<td>2.12 (9H, m, $\text{C}_4\text{H}_9$), 1.52 (3H, d, CH$_3$), 5.64 and 5.92 (1H, s, s, 3α or β-H), 7.97 (4H, m, $\text{C}_6\text{H}_4$)</td>
<td>81</td>
</tr>
<tr>
<td>7l</td>
<td>$\text{C}<em>{12}\text{H}</em>{17}\text{BrOTe}$</td>
<td>116-118</td>
<td>2.01 (9H, m, $\text{C}_4\text{H}_9$), 1.47 (3H, d, CH$_3$), 5.48 and 5.75 (1H, s, s, 3α or β-H), 7.84 (4H, m, $\text{C}_6\text{H}_4$)</td>
<td>85</td>
</tr>
<tr>
<td>7m</td>
<td>$\text{C}<em>{12}\text{H}</em>{17}\text{IOTe}$</td>
<td>120-121</td>
<td>-</td>
<td>62</td>
</tr>
<tr>
<td>7n</td>
<td>$\text{C}_{13}\text{H}_8\text{O}_3\text{Te}$</td>
<td>68-71</td>
<td>1.78 (9H, m, $\text{C}_4\text{H}_9$), 2.01 (3H, s, CH$_3$), 5.40 (2H, dd, $J = 15.1$ Hz, 3-H), 7.53 (4H, m, $\text{C}_6\text{H}_4$)</td>
<td>50</td>
</tr>
<tr>
<td>7o</td>
<td>$\text{C}<em>{22}\text{H}</em>{30}\text{O}_3\text{Te}_2$</td>
<td>89-91</td>
<td>1.92 (9H, m, $\text{C}_4\text{H}_9$), 5.40 (2H, dd, $J = 15.2$ Hz, 3-H), 7.65 (4H, m, $\text{C}_6\text{H}_4$)</td>
<td>32</td>
</tr>
</tbody>
</table>
In contrast with similar sulfurane \textsuperscript{16}, no diastereotopic splitting has been observed for the methylene protons of \textsuperscript{13} at ambient temperature \textsuperscript{14}. This fact indicates that the energy barrier to the polytopal rearrangement of the tellurane is lower than that of its sulfur analogue and is in accord with the predictions based on the quantum mechanical calculations \textsuperscript{17}.

Oxatelluroles \textsuperscript{1} and benzooxatelluroles \textsuperscript{7} are susceptible to readily occurring exchange of the halogen atoms at the tellurium centers for other anionic groups \textsuperscript{9}. When treated with potassium iodide in an acetone solution, the compounds \textsuperscript{1d,f} are converted to the corresponding iodo derivatives (the yields are 80-85\%). 1-Acetoxy-1-butyl-2,1-benzoxatellurole \textsuperscript{7n} was obtained by the reaction of its bromo analogue with silver acetate. Contrary to expectations, the action of an ethanol solution of NaOH on \textsuperscript{7b} leads not to 1-butyl-1-hydroxybenzotellurole-2,1, but to a product of its dehydration \textsuperscript{7o} \textsuperscript{9}.

The halogen exchange in the compounds \textsuperscript{7} may also be realized through their reduction with zinc powder followed by a treatment of the reaction mixture with an equivalent amount of halogen \textsuperscript{9}. Thus, the compound \textsuperscript{7c} was prepared in almost quantitative yield from the bromo derivative \textsuperscript{7b}.

\textit{o-Carbonyl derivatives of Te,Te-dibromophenylbutyl telluride \textsuperscript{14a-c} are formed in 73-95\% yields when chloroform or carbon tetrachloride solutions of 1-bromo-1-butyl-2,1-benzoaxatelluroles \textsuperscript{7b,f,i} and an equimolar amounts of bromine are heated at reflux\textsuperscript{9,12,13}. A possible mechanism of this Te-O bond cleavage reaction involves the derivatives of hexacoordinated tellurium \textsuperscript{15} rearranging to the hypobromites \textsuperscript{16}.}
Treatment of 7b with excess bromine in acetic acid solution results in formation of 2-tribromotellurobenzaldehyde 17 in 63% yield. The initially formed aldehyde 14a eliminates a molecule of butyl bromide to give the tellurenyl bromide 18 which is readily oxidized by bromine affording the tellurium tribromide 17 as the final product.

With 1-bromo-1-butyl-3-methyl-2,1-benzoxatellurole 7l, this reaction leads not only to the ketone 19a, but also 19b. When two moles of bromine are used, the ω,ω-dibromoacetophenone 19a has also been found among the products of the reaction.

The reactions above described represent a new convenient method specific to organotellurium compounds for the conversion of o-alkyltellurobenzaldehydes into o-alkyltellurobenzophenones, and o-alkyltellurobenzylic alcohols into o-alkyltellurobenzaldehydes. It is worth noting that the attempts to directly oxidize 1-(2’-methyltellurophenyl)ethanol-1 into the corresponding derivatives of acetophenone failed.
2. 2,1-Oxatellurol-3-ones

The methods developed for the synthesis of oxatelluroles and benzoxatelluroles have been found to be applicable for the synthesis of their oxo-derivatives 5, 6. Thus, 1-aryl-1-chloro-2,1-benzoxatellurole-ones-3 were prepared in 75-90% yields by oxidation of 2-carboxydiphenyl telluride with tert-butylhypochlorite and the dehydrohalogenation of 2-(dichlorotelluroaryl)benzoic acids under the action of triethylamine.

The dihydro derivatives of the oxatellurolones were obtained in high yields (more than 90%) by oxidation of β-aryltelluropropionic acids with tert-butylhypochlorite in chloroform solution. The bromo analogues of 6 are accessible through dehydrobromination of aryl(β-carboxyethyl)tellurium dibromides in toluene solution.

Benzoxatelluro-3-ones 5 are isoelectronic to 2-phenyliodonium carboxylates. One may expect that by this analogy thermolysis of 5 would lead to the formation of dehydrobenzene and aryltellurenyl chlorides, which in their turn would disproporionate into diaryltellurium dichlorides and Te. However, no dehydrobenzene was generated in this reaction were performed under various conditions.
3. Isotellurazoles and N-arylisotellurazolium cations

Isotellurazoles 2 were first prepared by the reaction between $\alpha$-acetylenic ketones, potassium telluride and hydroxylamine-O-sulfonic acid occurring in an aqueous solution of potassium acetate $^3$. The compounds 2 are formed in very low yields (less than 10%). The method cannot be applied for the synthesis of 3H-isotellurazoles because when $\alpha$-acetylenic aldehydes are used in this reactions instead of the ketones, only di($\beta$-cyanovinyl)tellurides are formed as the final products$^3$.

We have found that $\beta$-bromotellurenylvinylaldehydes $^7,8$ 20 may serve as the precursors of isotellurazoles when reacted with ammonia in a benzene solution. In this way, 4,5-tetramethyleneisotellurazole 2a was obtained in 70% yield $^{22}$. The reaction proceeds through dehydrobromination of the intermediate imine 21.

\[ \begin{align*}
\text{CHO} & \quad + \text{NH}_3 \\
\text{TeBr} & \quad \rightarrow \quad \text{CH}=\text{NH} \\
20 & \quad \rightarrow \quad \text{TeBr} \\
\text{-H}_2\text{O} & \quad \text{NH}_3 \\
\text{-NH}_4\text{Br} & \quad 2a
\end{align*} \]

Preparation of the compounds 20 is difficult $^{7,8}$, however the readily accessible $\beta$-methyldibromotellurovinylaldehydes 22 have been found to be useful precursors of isotellurazoles.

By bubbling ammonia through benzene solutions of the tellurium dibromides 22 isotellurazoles 2a,b were obtained in about 70% yields. In accordance with these findings $^{23}$, the following mechanism has been suggested for this reaction.

\[ \begin{align*}
\text{R}^1\text{R}^2\text{CHO} & \quad + \text{NH}_3 \\
\text{TeMeBrBr} & \quad \rightarrow \quad \text{R}^1\text{R}^2\text{CH}=\text{NH} \\
22 & \quad \rightarrow \quad \text{R}^1\text{R}^2\text{TeMeBr} \\
\text{-H}_2\text{O} & \quad \text{-MeBr} \\
\text{-NH}_4\text{Br} & \quad 21 \\
\text{NH}_3 & \quad \text{NH}_4\text{Br} \\
\text{R}^1 & = 4-\text{BrC}_6\text{H}_4, \quad \text{R}^2 = \text{H} \quad \text{(b)}
\end{align*} \]
An analogous route has been previously used for the synthesis of isoselenazoles \(^{24}\). However, due to low thermal stability of the tetracoordinated selenium analogues of \(22\) the reaction must be carried out at very low temperature \((-70^\circ C)\). Likewise benzoisotellurazole, isotellurazoles \(2\) react with methyl iodide under mild conditions to give the quaternary salts, e.g. \(24\), in good yields \(^{22}\). N-Arylisotellurazolium perchlorates \(25\) \(^{22}\) and their benzoderivatives \(25\) \(\left(R^1+R^2 = (CH=CH)_2\right)\) \(^{23,25}\) were prepared in high yields by treating solutions of \(\beta\)-bromotellurenylvinylaldimines \(26\) \(\left(X = Br\right)\) \(^{22}\) and 2-chlorotellurenylbenzaldimines \(26\) \(\left(26, \; R^1 + R^2 = (CH=CH)_2, \; X = Cl\right)\) \(^{25}\) with silver perchlorate in acetone or dimethylformamide.

\[
\begin{align*}
\text{R}^1 = 4-\text{BrC}_6\text{H}_4, \; \text{R}^2 = \text{H}: \; \text{Ar} = 4-\text{MeC}_6\text{H}_4 \; \text{(a)}, \; 4-\text{MeOC}_6\text{H}_4 \; \text{(b)}; \; \text{R}^1 + \text{R}^2 = (\text{CH}_2)_4: \; \text{Ar} = 4-\text{MeC}_6\text{H}_4 \; \text{(c)}, \; 4-\text{MeOC}_6\text{H}_4 \; \text{(d)}; \; \text{R}^1 + \text{R}^2 = (\text{CH=CH})_2: \; \text{Ar} = \text{Ph} \; \text{(e)}, \; 4-\text{MeC}_6\text{H}_4 \; \text{(f)}, \; 4-\text{BrC}_6\text{H}_4 \; \text{(g)}
\end{align*}
\]

4. 2-Aroyl-1,2,3-telluradiazines

Dehydrobromination of the arylhydrazons of \(\beta\)-bromotellurenylvinylaldehydes \(27\) gives rise to previously unknown 1,2,3-telluradiazines \(28\) \(^{26}\). As shown by scheme below, the formation of \(28\) in the reaction of the aldehydes \(22\) with the hydrazides proceeds with elimination of a molecule of an alkyl bromide. The heterocycles \(28\) are obtained in rather high yields (about 80%).

\[
\begin{align*}
22 \; \text{R} = \text{Me}, \; \text{R}^1 + \text{R}^2 = (\text{CH}_2)_4; \; \text{R} = \text{Bu}, \; \text{R}^1 + \text{R}^2 = (\text{CH}=\text{CH})_2 \\
27,28 \; \text{R}^1 + \text{R}^2 = (\text{CH}_2)_4: \; \text{Ar} = 4-\text{MeOC}_6\text{H}_4 \; \text{(a)}, \; 4-\text{BrC}_6\text{H}_4 \; \text{(b)}; \; \text{R}^1 + \text{R}^2 = (\text{CH}=\text{CH})_2: \; \text{Ar} = 4-\text{MeOC}_6\text{H}_4 \; \text{(c)}
\end{align*}
\]

5. 1,2,6-Benzoxatellurazocines

Preparation of 1,2,6-benzoxatellurazocines \(29\) \(^{27}\) is another example of the use of the reaction of dehydrobromination of tellurenylbromides in the synthesis of tellurium-containing heterocycles. 2-Bromotellurenylcyclohexenylidene-2'-aminophenols \(30\), were used as the starting material. A treatment of suspensions of \(30\) in benzene with equimolar amounts of triethylamine followed by short reflux of the reaction mixtures resulted in the compounds \(29\) obtained in 80-90% yields.
\[
\begin{align*}
\text{CHO} & \quad + \quad \text{H}_2\text{N}-\text{R} \quad \xrightarrow{\text{MeOH}/\Delta} \quad \text{C}=\text{N} \quad \xrightarrow{\text{Et}_3\text{N}} \\
\text{Br} & \quad \text{TeMeBr} & \quad \text{HO} \quad \text{R}^1 \quad \text{R} & \quad \text{Br} & \quad \text{R}^1 \\
\text{30a-c} & \quad \text{Et}_3\text{N.HBr} & \quad \text{30a-c} \\
\text{29a-c} & \\
\end{align*}
\]

29, 30 R = R\(^1\) = H (a); R = Me, R\(^1\) = H (b); R = H, R\(^1\) = NO\(_2\) (c)

References