

# Synthesis of organotellurium compounds by transmetallation reaction of organomercury compounds / review

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## ABSTRACT

Synthetic organotellurium compounds have increased markedly recently as a result of their important applications in different fields, including synthetic intermediates, reagents, antioxidant agents, catalysts, antitumors, pharmaceutical agents, and organic synthesis, because the organotellurium group easily undergoes electrophilic or nucleophilic reactions. There are a variety of synthetic routes to prepare organotellurium compounds. In this review, we will discuss the method of preparing organic tellurium compounds using the transmetallation reaction of organomercury compounds. Using this method, many organic tellurium compounds based on amines, pyrazole, Schiff base, azo, and thiadiazole moiety were prepared, which may not be prepared by other methods.

## Keywords:

## Introduction

Tellurium is a stable and solid element lies after the selenium in the periodic table group 16 which called chalcogens. Te bears a lot of similarities with selenium in many of its properties and reactions. It is classified as a metalloid due to Te is properties that are intermediate between metals and nonmetals [1, 2]. Franz Joseph Müller von Reichenstein discovered it in 1782, 35 years before selenium was discovered [1]. Tellurium is less abundant in the Earth's crust than gold, platinum, or the so-called "rare-earth" metals (around 1 ppb)[3]. In nature, tellurium is a mixture of isotopes; those with a natural abundance 34.5% are <sup>130</sup>Te (2.5%), <sup>128</sup>Te (31.8%), <sup>126</sup>Te

(18.7%), <sup>125</sup>Te (7.0%), <sup>124</sup>Te (4.6%) and <sup>122</sup>Te (41%). Compounds including one or more tellurium atoms showed unique patterns in mass spectra as a result of this distribution. Importantly, the isotope <sup>125</sup>Te has nuclear spin (I = 1/2) of the nucleus which allows for NMR spectroscopic studies of tellurium compounds both in solution and in the solid state; the isotope <sup>123</sup>Te (abundant 0.9%) also has I = 1/2. The range of <sup>125</sup>Te NMR chemical shifts relative to Me<sub>2</sub>Te ( $\delta$  0 ppm), which range from around 1800 ppm for the telluride ion (Te<sup>-2</sup>) to around +3100 ppm for tellurium cations, makes it easier to identify tellurium in a variety of chemical environments, such as different oxidation states. Furthermore, the magnitude

of spin–spin coupling constants for  $^{125}\text{Te}$  and other spin 1/2 nuclei gives important bonding information. Tellurium exhibits a wide variety of oxidation states such as -1, -2, 0, +1, +2, +4 and +6 [4].

### Organotellurium compounds

Organotellurium compounds are classified into several classes. The main classes of organic tellurium compounds such as organytellurium monohalid ( $\text{RTeX}$ ), organytellurium trihalides ( $\text{RTeX}_3$ ), diorganytellurium dihalides ( $\text{R}_2\text{TeX}_2$ ), diorganyl tellurides ( $\text{R}_2\text{Te}$ ), diorganyl ditellurides ( $\text{R}_2\text{Te}_2$ ) and telluronium salts [ $\text{R}_2\text{R}'\text{Te}]^+ \text{X}^-$  [5-6].

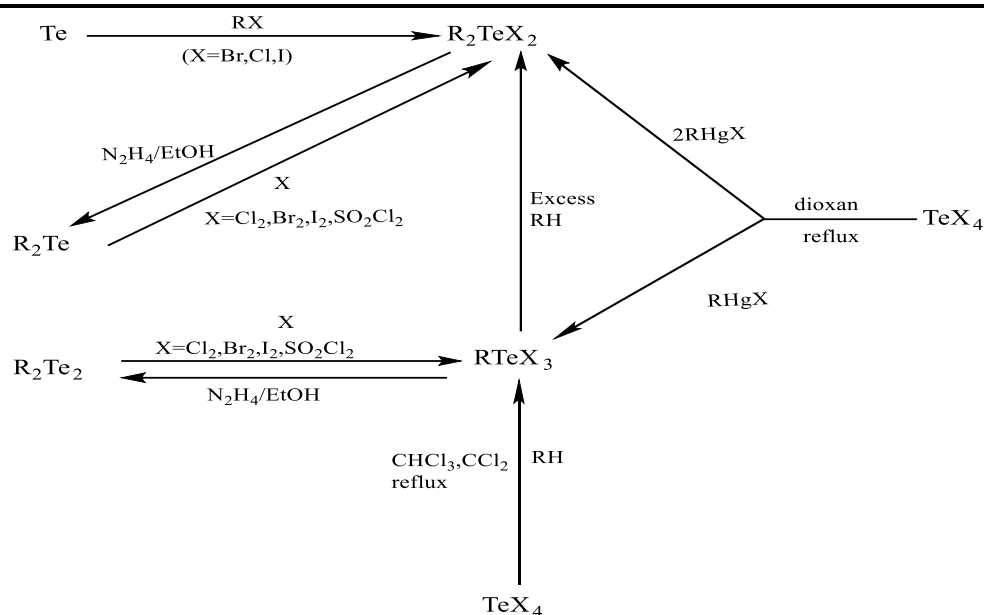
In the past, there has been an increase in the exploration of new organotellurium compounds, and as a result, a wide range of functionalized tellurium derivatives have been synthesized. [7–14]. These possess potential applications in the Organotellurium compounds have been mainly used as antioxidant agents [15-19] polymerization catalysts [20-22], antitumors and pharmaceutical agents [23,24], organic super conductors [25,7], synthetic intermediates [26,27], and as ligands with many transition metal ions [28-30], Organotellurium-mediated living radical polymerization [31].

Organotellurium compounds were also used as selective reduction reagents of functional groups[32], such as carbonyl group in aldehydes and ketones can be reduced to the corresponding primary and secondary alcohols

by  $\text{HTe}$  and  $\text{PhTeH}$ . Also  $\text{C}=\text{C}$  and  $\text{C}=\text{C}$  bonds conjugated to aromatic groups can be reduced to their corresponding saturated bonds by treatment with  $\text{PhTeH}$  or  $\text{NaHTe}$  [33,34]. The inorganic compounds of tellurium were used in photo cell [35], and in dry silver Processes [36]. Organotellurium compounds have received considerable interest in the industry field of nanoparticulate semiconductors[37,38] and as optical power limiting[39]. Organotellurium compounds are biologically important analytes and biologically active [40,41].

Tellurium is rarely non-toxic(elemental) in its natural condition. On account of the reducing electronegativity of the chalcogen, more shifts to tellurium and polonium, thus forming feeblish bonds inorganic chemical compounds[42,43]. Inorganic compounds, the carbon-tellurium ( $\text{C}-\text{Te}$ ) bond is weak and readily decomposes under the influence of water, light, and heat. [44,45] A variety of methods for the preparation of organotellurium compounds[46].

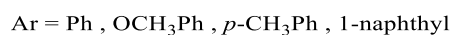
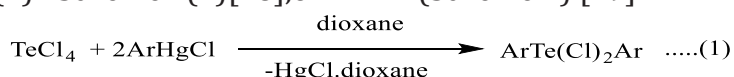
In this article, we will discuss the method of preparing organic tellurium compounds using the transmetallation reaction of organomercury compounds (scheme 1). Mercurated method was successfully employed in the synthesis of many organometallic compounds of transition metals which cant synthesis by the Grignard or lithiation reactions. [47]. Many researchers have used this method to synthesize new organic tellurium compounds.



(Scheme 1) : Some common synthetic routes to organytellurium compounds

The general procedure reaction  $\text{TeCl}_4$  with arylmercury (II) chloride under reflux in anhydrous dioxane gave diaryltellurium dichlorides equation (1) Scheme (2)[48], or

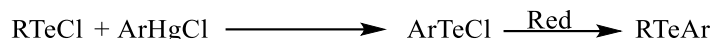
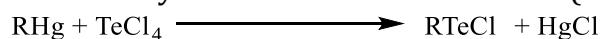
reaction diaryl mercury with elemental tellurium upon heating in absence of a solvent to produce diaryltelluride equation (2) (Scheme 2) [49].



(Scheme 2)

Organic mercury(II) halides were employed to prepare symmetrical and unsymmetrical

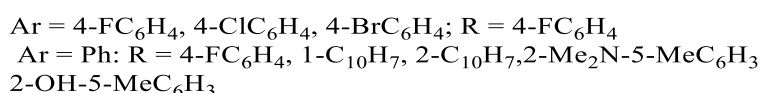
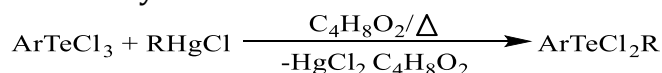
telluride by formation of organyl tellurium trichlorides(50) (Scheme 3).



(Scheme 3)

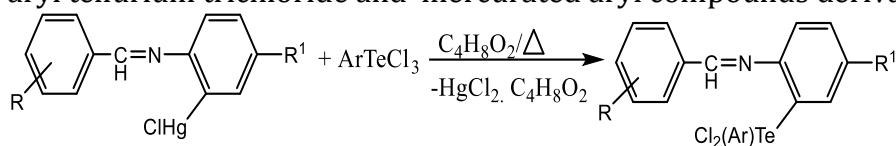
Many researchers synthesize unsymmetrical diorganytellurium dichlorides by the reaction

of  $\text{TeCl}_4$  with arylmercury chlorides, dioxane used as a solvent[50,51-53] (Scheme 4).



(Scheme 4)

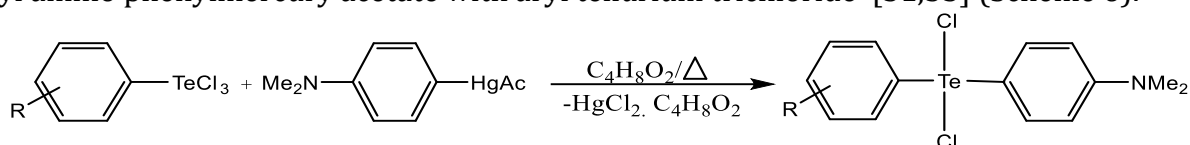
Wu *et al* [54] synthesized a organictellurium compounds containing azomethines moiety vie reaction between aryl tellurium trichloride and mercurated aryl compounds derivatives(Scheme 5)



Ar = EtOC<sub>6</sub>H<sub>4</sub>; R = H; R<sup>1</sup> = Me, MeO, Cl, Br; R = 4-MeO, 3-MeO, 2-MeO  
4-Cl, 3-Cl, 2-Cl, 4-Br, 3-Br, 4-NO<sub>2</sub>, 3-NO<sub>2</sub>

(Scheme 5)

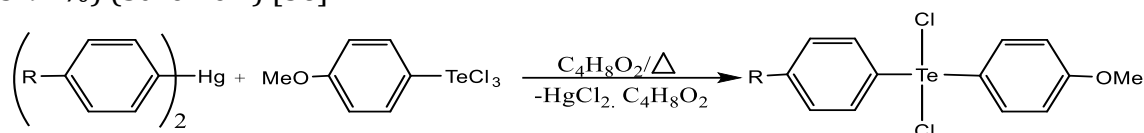
Asymmetric aryl(4-dimethylaminophenyl) tellurium dichlorides are prepared by reacting 4-dimethyl amino phenylmercury acetate with aryl tellurium trichloride [51,55] (Scheme 6).



R = H, 4-MeO, 4-EeO, 4-Phe, 4-Me, 4-Cl, 3-Cl, 2-Cl, 4-Br, 3-Br, 3-NO<sub>2</sub>, 4-F

(Scheme 6)

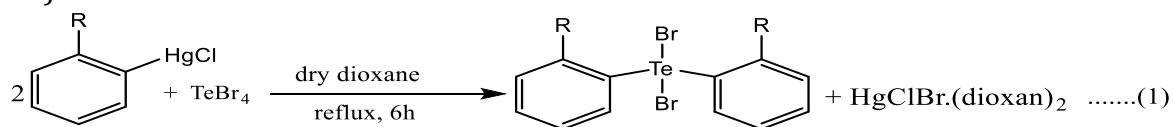
Reaction of aryltellurium trichlorides with TeCl<sub>4</sub> gave unsymetric diaryl tellurium dichloride in yields (93-97%) (Scheme 7) [56] .



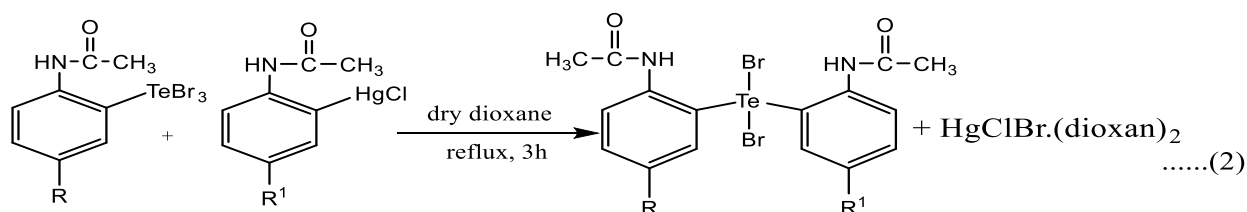
R = H, MeO

(Scheme 7)

Al-Rubaie *et al* [57, 58] synthesized diorganytellurium dihalides by reacted tellurium tetrahalides equation (1) (Scheme 8) or organytellurium trihalides with organomercuric chlorides equation 2 (Scheme 8)



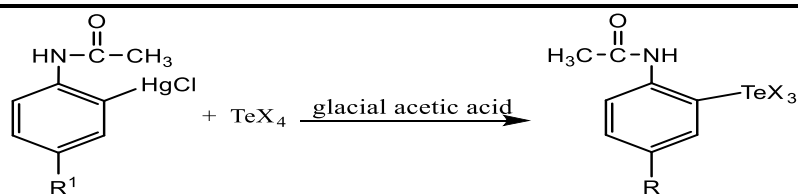
R = NH<sub>2</sub>, CH<sub>2</sub>OH



R = Br, NO<sub>2</sub>, CH<sub>3</sub>; R<sup>1</sup> = H, OH, OCH<sub>3</sub>, OEt

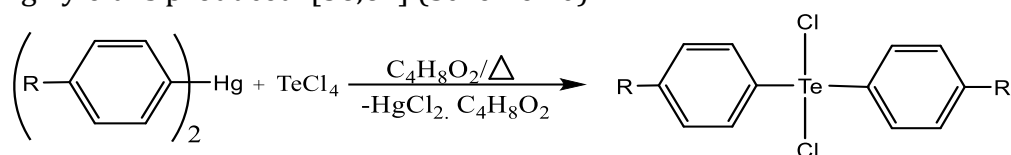
(Scheme 8)

Reaction of organomercuric chloride base on acetamido moiety with tellurium tetrahalide produced corresponding organotellurium trihalide derivatives, glacial acetic acid used as a solvent (Scheme 9). [59,60]



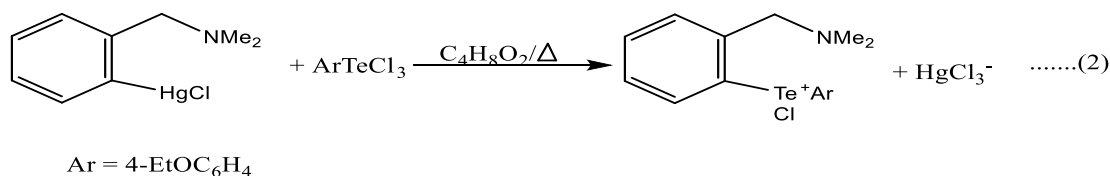
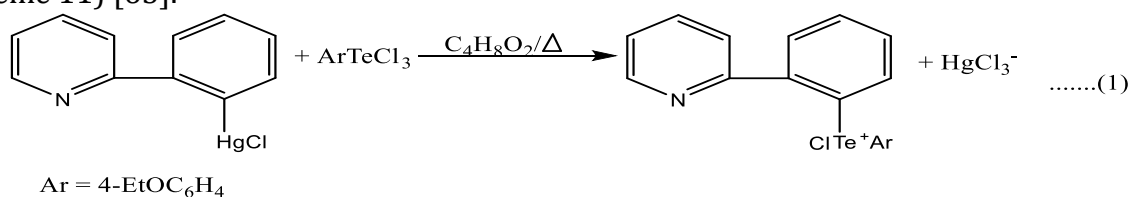
(Scheme 9)

By reacting diarylmercury derivatives with  $\text{TeCl}_4$  in a dry dioxane solvent, symmetric diaryltellurium dichloride in high yield is produced. [56,61] (Scheme 10).



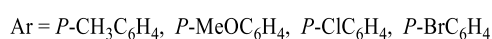
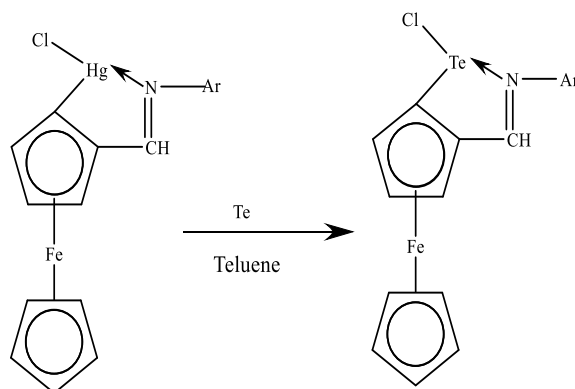
(Scheme 10)

telluronium salts (2-(2'-Pyridyl) phenylmercuric chloride in 67% yield) obtained via the reaction of Intramolecularly N-Hg coordinated arylmercuric chloride with aryltellurium trichloride equation (1) (Scheme 11) [62]. In addition, a 51% yield of telluronium salts was obtained by reacting 4-ethoxyphenyl tellurium trichloride with 2-dimethylaminomethylphenylmercuric chloride (equation (2)) (Scheme 11) [63].



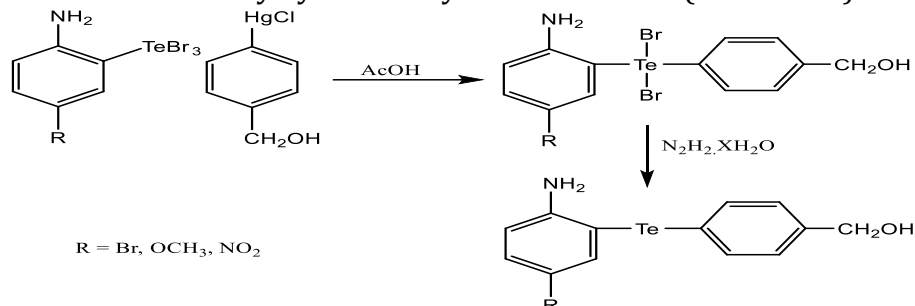
(Scheme 11)

Yang and coworkers [64] prepared a novel of ferrocenyliminestellurenyl chloride by reacting tellurium powder with ferrocenylimines mercuric chloride in toluene solvent to afford the tellurenyl chloride, (Scheme 12).



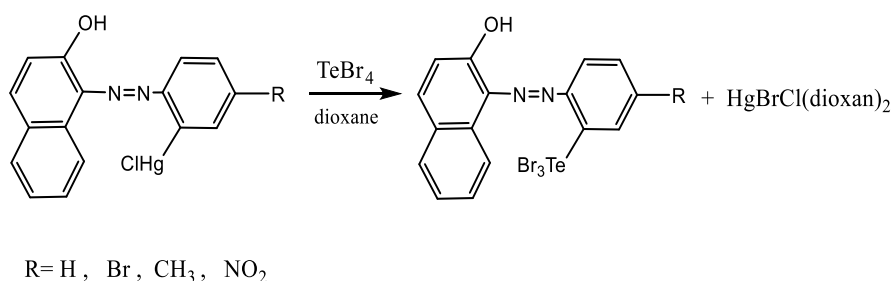
(Scheme 12)

Al-Rubaie *et al* [65] prepared a novel unsymmetrical tellurides from the reaction of 4-hydroxy methyl phenyl mercury chloride with the corresponding 2-amino aryl telluride tribromide in glacial acetic acid and followed reduction by hydrazine hydrate in ethanol (Scheme 13).



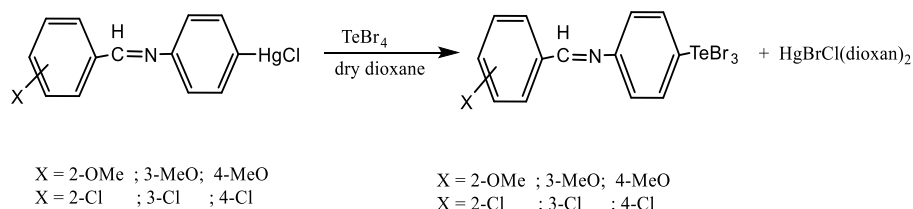
(Scheme 13)

Al-Fregi *et al* synthesized [66,67] 2-(2-hydroxynaphthylazo)-5-substituted phenyltellurium tribromides by reaction of corresponding aryl mercury chloride with TeBr<sub>4</sub> in a ratio of 1:1 mole and dry dioxane, (Scheme 14).



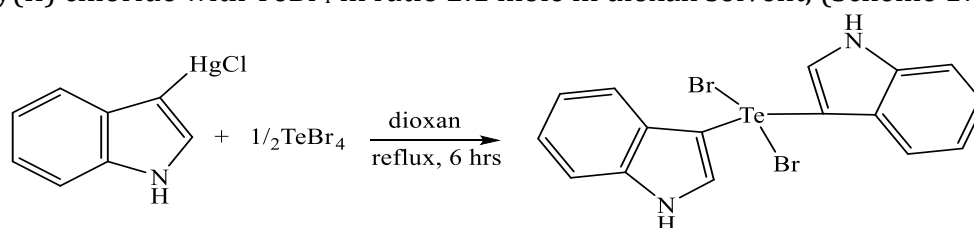
(Scheme 15)

Tellurated schiff bases are formed by the reaction of tellurium tetrabromide with organomercuric chloride containing azomethine moiety synthesis and in the ratio of 1:1 mole (Scheme 16) [67].



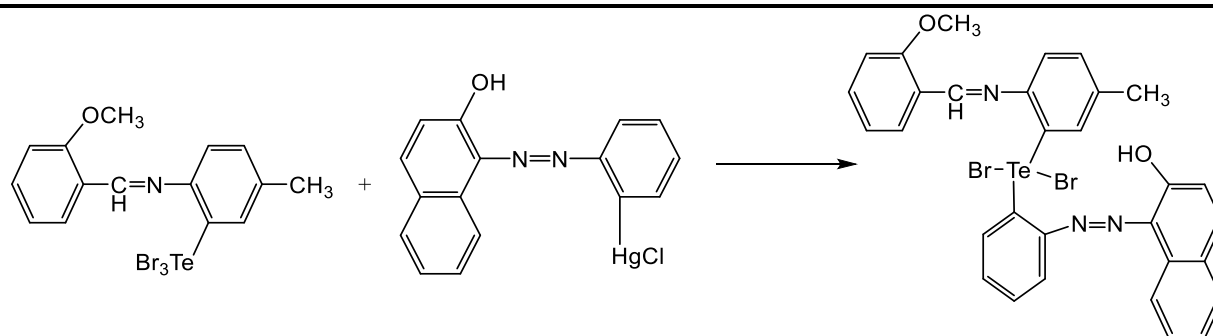
(Scheme 16)

Al-Fregi *et al* [68] synthesized bis[3-indolyl] tellurium bromide by refluxing of 3-indolylmercury(II) chloride with TeBr<sub>4</sub> in ratio 2:1 mole in dioxan solvent, (Scheme 17).



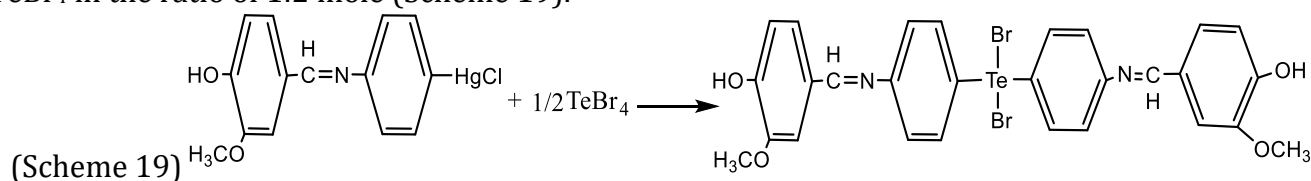
(Scheme 17)

Reaction of 2-(2-hydroxynaphthylazo) phenylmercuric chloride with 2-(2-methoxy benzylidene amino)-5-methyl phenyl tellurium tribromide produced [2-(2-hydroxynaphthylazo) phenyl][2-(2-methoxybenzylidene amino)-5-methylphenyl] tellurium dibromide (Scheme 18) [69].



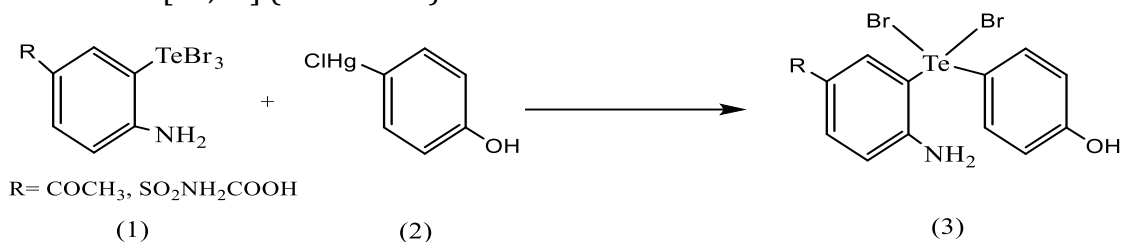
(Scheme 18)

Al-Jadaan *et al* [70] prepared bis 4-[4'-hydroxy-3'-methoxy benzylidene aminophenyl] tellurium dibromide by the reaction of 4-[4'-hydroxy-3'-methoxybenzylidene aminophenyl]mercuric chloride with TeBr<sub>4</sub> in the ratio of 1:2 mole (Scheme 19).



(Scheme 19)

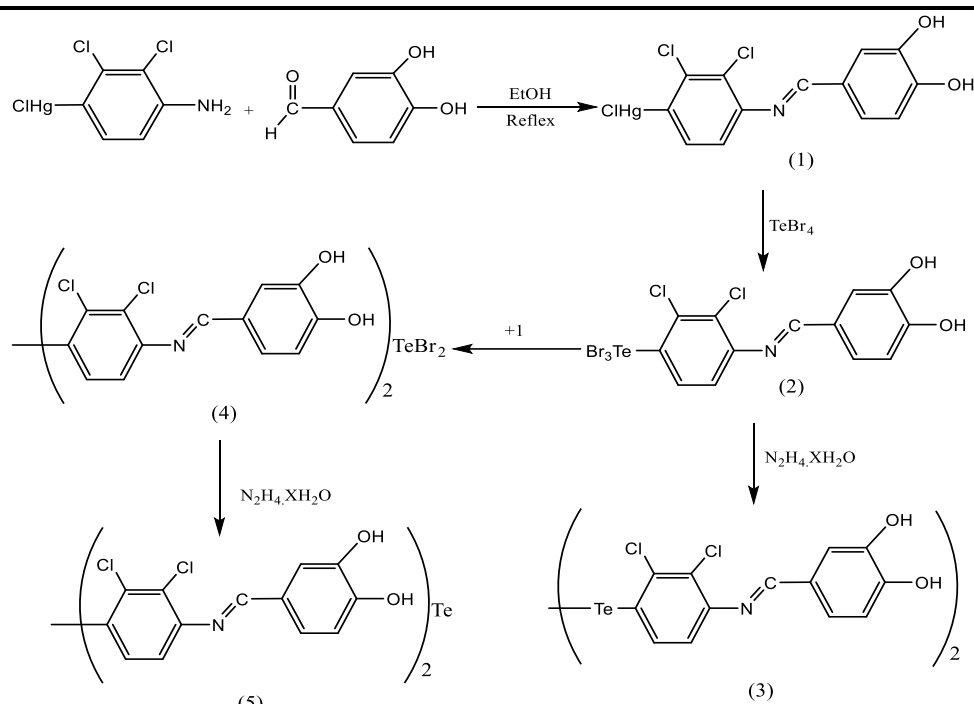
Reaction of aryltellurium trihalides derivatives (1) with (4-hydroxyphenyl)mercury chloride (2) gave a new unsymmetrical organotellurium compound (3) in a 1:1 mole ratio in dry chloroform solvent and 4h reflux [71,72] (Scheme 20).



(Scheme 20)

Al-Asadi and coworkers [73] synthesized new organomercury and organotellurium compounds. Mercureted shiff base (1) was produced by reacting 3,4-dihydroxy benzaldehyde with 4-amino-2,3-dichlorophenyl mercuric chloride. Tellurated of compound (1) by TeBr<sub>4</sub> produced ortho tellurated shiff base (2). The reaction compound (2) with (1) gave symmetric diaryl

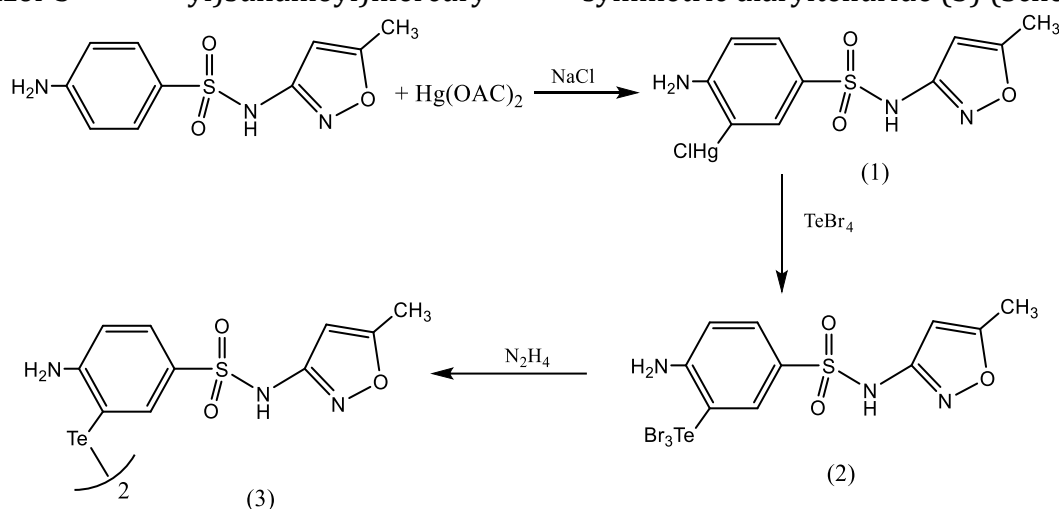
dibromidetelluride (4). Diaryl ditelluride (3) and diaryl telluride (5) are formed by the reaction of compounds (2) and (4) with ethanolic hydrazine (Scheme 21). The antioxidant activity and antibacterial properties of synthesized compounds were studied. Compounds (2) and (4) showed higher activity than other compounds.



(Scheme 21)

AL-Jadaan [74] synthesized (2-Amino-(N-(5-methylisooxazol-3-yl)sulfamoyl)tellurium tribromide (2) by reacted 2-amino-(N-(5-methylisooxazol-3-

chloride(1) with  $\text{TeBr}_4$  in ratio 1:1 mole followed reaction compound (2) with hydrazine hydrate in ethanol produced new symmetric diaryltelluride (3) (Scheme 22)

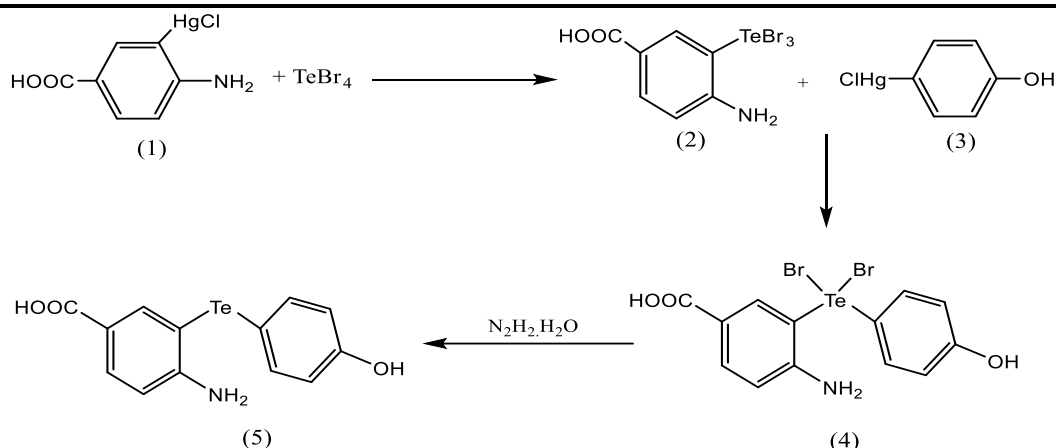


(Scheme 22)

2-Amino-5-carboxyphenyl tellurium tribromide (2) is formed by the reaction of 2-amino-5-carboxyphenyl mercury (II) chloride (1) with  $\text{TeBr}_4$ . Reaction of compound (2) with 4-hydroxyphenyl mercury chloride (3) to produce 4-hydroxyphenyl-2-amino-5-

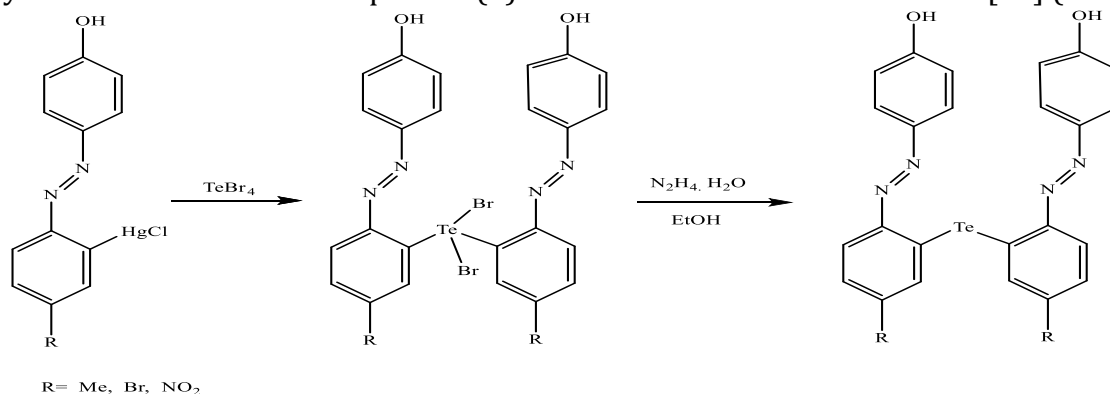
carboxyphenyl tellurium dibromide (4) followed by reduction with ethanolic hydrazine hydrate ( $\text{N}_2\text{H}_4.\text{H}_2\text{O}$ ) produced the corresponding asymmetrical telluride (5) (Scheme 23). Compound (5) showed antioxidant and antitumor activity [71].





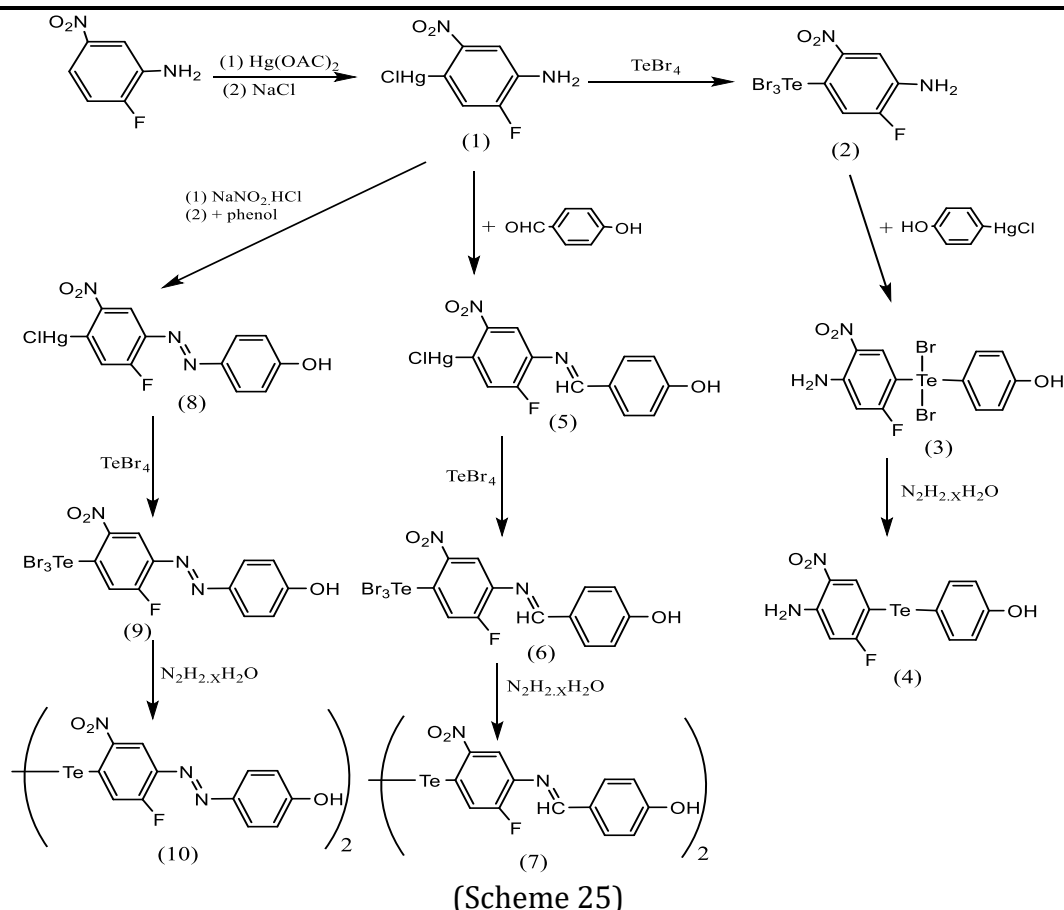
Reaction of 2-(4-hydroxyphenylazo)aryl mercuric chloride (1) with  $\text{TeBr}_4$  to afford symmetric bis(2-(4-hydroxyphenylazo)-5-methylphenyl) tellurium dibromide compound (2) in dry dioxane solvent. Compound (2)

followed by reduction with hydrated hydrazine ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ) produced a symmetrical telluride compound (3). Compound (3) showed good antibacterial activity against *Staphylococcus aureus* and *E. coli* bacteria. [75] (Scheme 24)



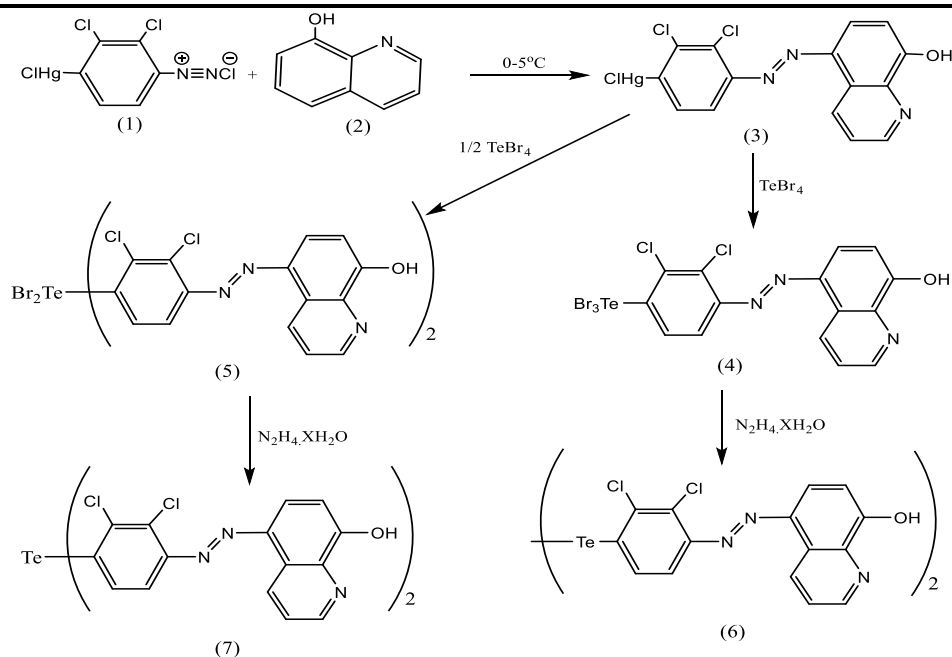
Transmetallation reaction of aryl mercuric chloride (1) with  $\text{TeBr}_4$  gave (4-amino-5-fluoro-2-nitrophenyl) tellurium tribromide (2). Reaction of 4-hydroxyphenyl mercuric chloride with compound (2) to afford diaryltellurium dibromide (3). Reaction of compound (1) with 4-hydroxy benzaldehyde led to the new organomercury compound (5), while reaction of compound (1) with phenol produced a new organomercury compound containing an azo group (8). Aryltellurium

tribromide compounds (6) and (9) were obtained by reacting tellurium tetrabromide with compounds (5) and (8), respectively. Reduction of compounds (6) and (9) by ethanolic hydrazine gave diaryl ditelluride compounds (7) and (10), respectively. The new prepared compounds showed highly antibacterial activity against *Escherichia coli*, *Pseudomonas spp.*, *pneumonia*, *Proteus*, *Klebsiella*, and *Staphylococcus aureus* [76].



Reaction of 1-(4-mercury chloride-2,3-dichlorophenyl)-2-chloro diazin (1) with 8-hydroxyquinoline (2) gave a new organomercury (II) compound (3). Reaction of compound (3) with  $\text{TeBr}_4$  in ratio 1:1 and 1:2 mole led to tellurated azo compounds  $\text{ArTeBr}_3$  (4) and  $\text{Ar}_2\text{TeBr}_2$  (5), respectively. Later reduction of A compounds (4) and (5) by hydrazine hydrate in ethanol produced the

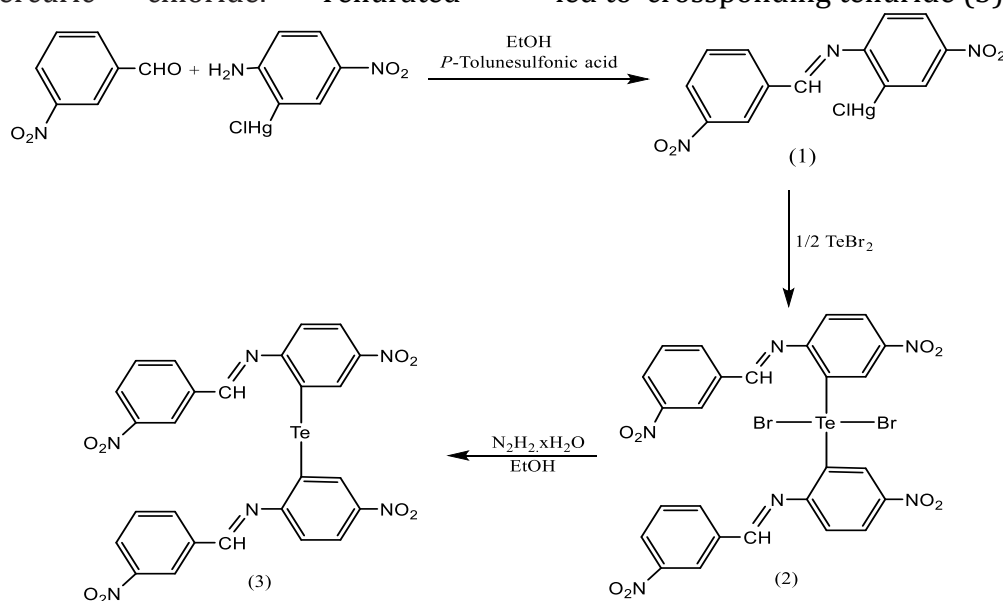
ditelluride (6), and telluride (7), respectively (Scheme 26). The antibacterial and antifungal activities of these compounds were studied. The synthesized compounds showed activity against *Aspergillus multi*, *Salmonella spp.*, *Staphylococcus aureus*, *Klebsiella pneumonia*, *Bacillus subtilis*, *Streptococcus spp.*, *Candida sp.*, *E. coli*, *Bacillus cereus.*, and *Aspergillus niger*. [77].



(Scheme 26)

Al-Fregi *et al* [78] prepared 2-(3-nitrobenzylideneamino)-5-nitrophenylmercuric chloride (1) via reaction of 3-nitro benzaldehyde with 2-amino-5-nitrophenylmercuric chloride. Tellurated

compound (1) with tellurium tetrabromide in a ratio of 2:1 mole produced the Schiff base tellurium dibromide (2). Reduction of compound (2) by ethanolic hydrazine hydrate led to crossponding telluride (3) (Scheme 27).

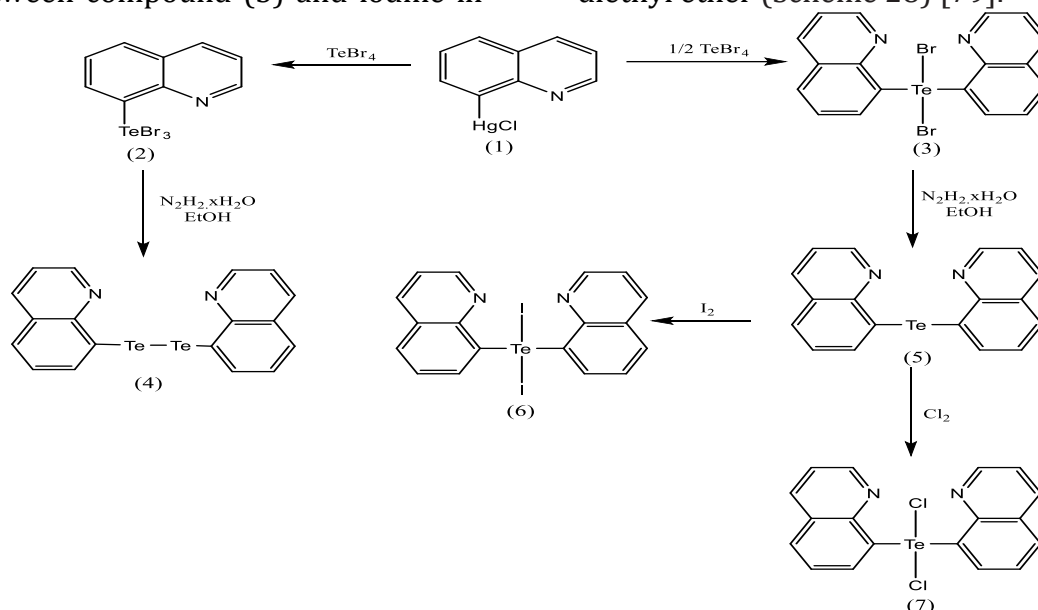


(Scheme 27)

Reaction of 8-(quinolyl) mercury(II) chloride (1) with  $\text{TeBr}_4$  in ratio 1:1 and 1:2 mole gave 8-(quinolyl)tellurium tribromide (2) and symmetrical bis[8-(quinolyl)]tellurium dibromide (3), respectively, Reduction of compounds (2) and (3) by hydrazine hydrate in

ethanol led to corresponding ditelluride (4) and telluride (5), respectively. Bis[8-(quinolyl)tellurium dichloride (6) produced direct reaction between compound (5) and Thionyl chloride in dry ether. Bis[8-(quinolyl)tellurium diiodide (7) obtained direct

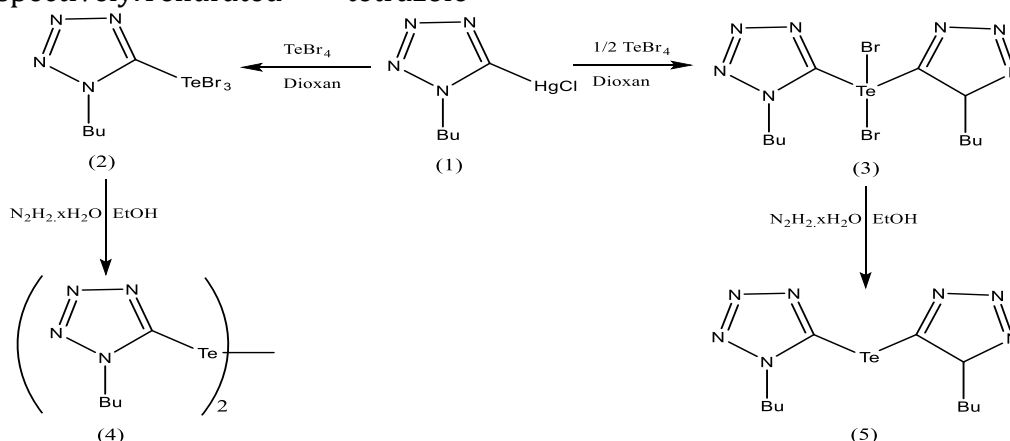
reaction between compound (5) and iodine in diethyl ether (Scheme 28) [79].



(Scheme 28)

New organotellurium compounds (1) and (2) with tetrazole rings were synthesized by reacting Tellurium tetrabromide with mercurated tetrazole (1) in 1:1 and 1:2 molar ratios, respectively. Tellurated tetrazole

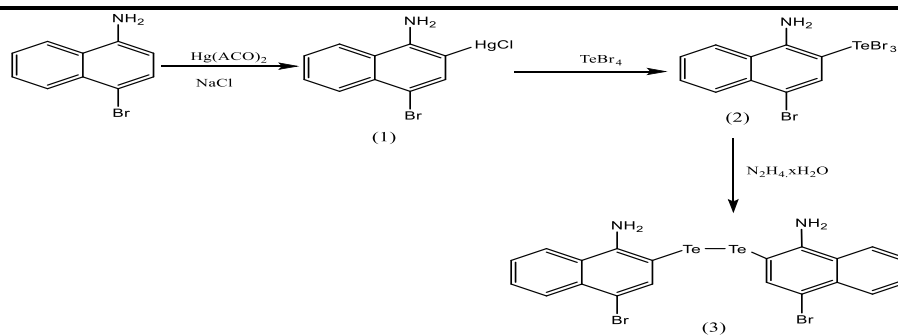
compounds (3) and (4) were redacted by ethanolic hydrazine to produce ditetrazole ditelluride (5) and ditetrazole telluride (6), respectively (Scheme 29) [80].



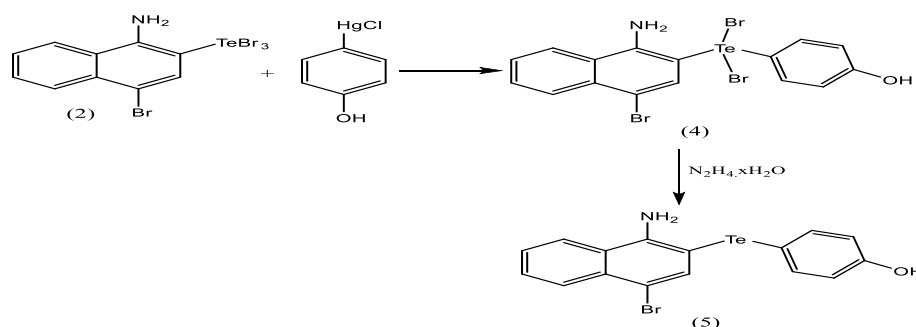
(Scheme 29)

Al-Asadia [81] synthesized a new series of organic tellurium compounds containing a naphthalene derivative. 4-Bromo-2-(tribromo- $\lambda^4$ -1-amine (2) obtained via reacted (1-amino-4-bromonaphthalen-2-yl)-mercuric chloride (1) with tellurium tetrabromide. Redaction of compound (2) by ethanolic hydrazine gave symmetrical ditelluride (3) (Scheme 30). Reaction of hydroxyphenyl mercuric chloride with compound (2) gave

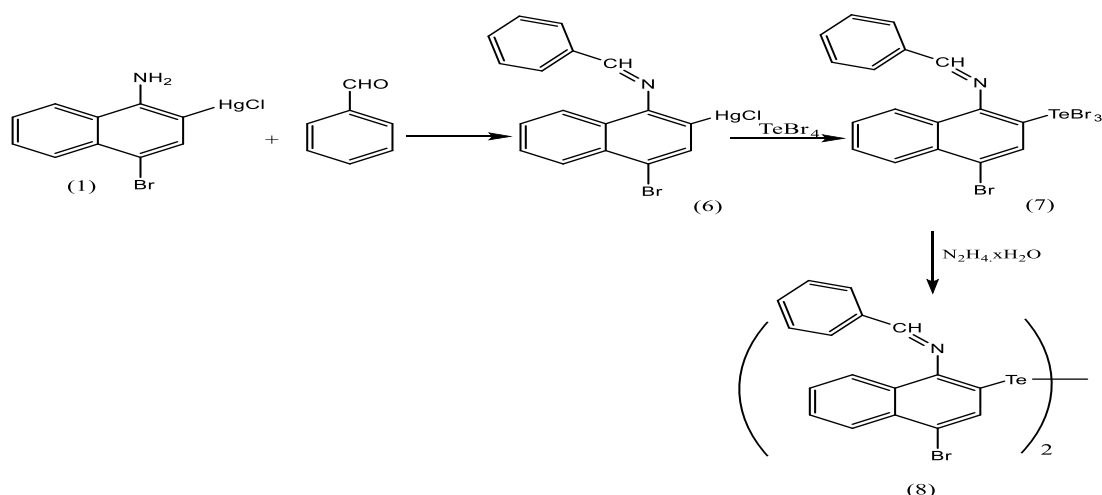
unsymmetrical diorganyl tellurium dibromide (4). Redaction of compound (4) by ethanolic hydrazine gave unsymmetrical telluride (5) (Scheme 31). Reaction compound (1) with benzaldehyde has produce compound (6). Last reaction compound (6) with  $\text{TeBr}_4$  in ratio 1:1 mole gave a new organotellurium tribromide (7) followed reduction compound (7) by hydrazine hydrate in ethanol gave new symmetrical diaryltelluride (8) (Scheme 32).



(Scheme 30)



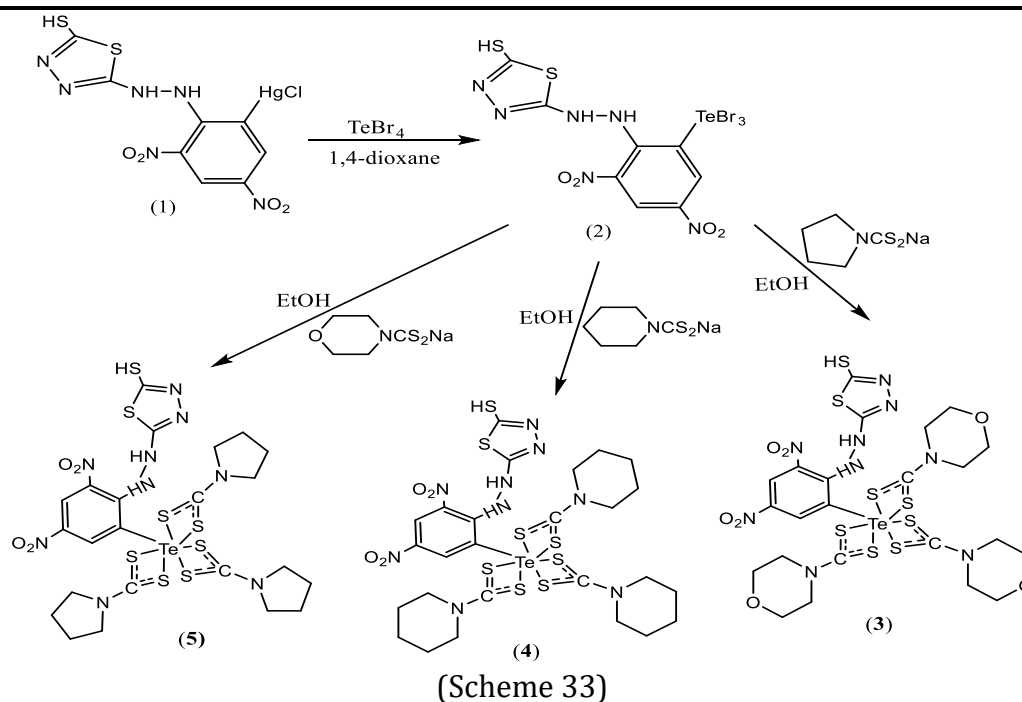
(Scheme 31)



(Scheme 32)

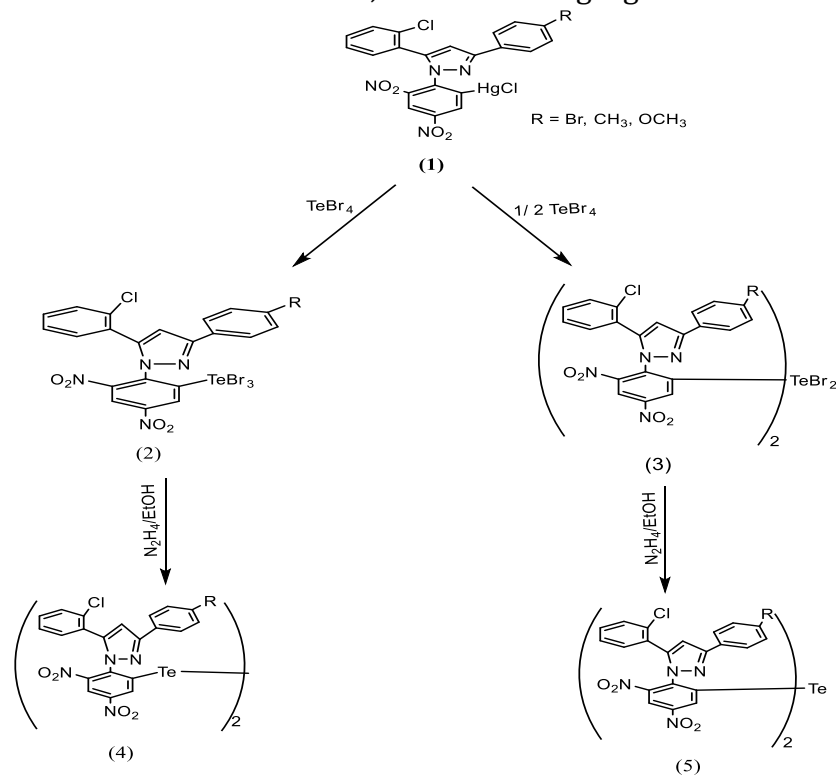
Sabti *et al* synthesized new organotellurium compounds based on the thiadiazol moiety  $\text{ArTeBr}_3$  (2) by reaction (2-(2-(5-mercapto-1,3,4-thiadiazol-2-yl)hydrazinyl)-3,5-dinitrophenyl) mercury chloride (1) with  $\text{TeBr}_4$  in a 1:1 mole ratio. Reaction compound (2)

with sodium phenyl thiocarbamate derivatives in 1:3 mole ratio gave crossponding compounds(3), (4) and (5) (Scheme 33). These compounds showed good activity in inhibiting the growth of *Staphylococcus aureus* and *Escherichia coli* bacteria [78].



Few studies on the synthesis of organotellurium compounds containing a pyrazole moiety have been published [83,84]. Sabti *et al* [85] synthesis tellurided pyrazole ( $\text{ArTeBr}_3$  (2) and  $\text{Ar}_2\text{TeBr}_2$  (3)) by reaction aryl mercury chlorides (1) with tellurium tetrabromide (Schem 34) in two mole ratio 1:1 and

respectively. Reduction compounds (1) and (2) by ethanolic hydrazine hydrate obtained  $\text{Ar}_2\text{Te}_2$  (4) and  $\text{Ar}_2\text{Te}$  (5), respectively. The biological activity of the synthesized compounds was studied against bacteria and fungals. The tellurated pyrazole compounds displayed inhibitory activity against bacterial and fungal growth.



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