REACTION OF POTASSIUM TELLUROCYANATE WITH 2-CHLOROETHANOL

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(Accepted for publication: June 9, 2013)

ABSTRACT

Reaction of 2-chloroethanol with potassium tellurocyanate gave a new heterocycle namely 1,3-oxatellura-2-imine 1 in a good yield. Halogenation of organotelluride 1 with $SOCl_2$, bromine and iodine gave dichloro, dibromo and diiodo organic tellurium compounds, Treatment of 1 with alkyl halides gave new organic tellurium compounds. Hydrolysis of 1 afforded a new cyclic telluride. All the new synthesized compounds were characterized by elemental analysis (CHN), IR, ^1H and ^{13}C NMR spectra

Keywords: Potassium tellurocyanate, 2-Chloroethanol, Cyclic telluride, Cyclization

INTRODUCTION

The biological importance of tellurium has attracted considerable attention as evidenced by several model studies on the antioxidant properties of synthetic organotellurium compounds [Engman *et al*,1992**]**.

Potassium or sodium tellurocyanate is a very useful reagent for the preparation of organic tellurocyanates [Bergman**,**1972**]**. The organic tellurocyanates (RTeCN) are less known compared with organic selenocyanates [Toshimitsu *et al*, 1987]. The first example of an organic tellurocyanate seems to be 1-azulenyl-tellurocyanate which was prepared by Nevedov [Nevedov *et al*,1968] in 1968, from the reaction of azulene in presence of coppre (II) acetate and potassium tellurocyanate (KTeCN) in acetonitrile.

Thibaut *et al* developed a new method for the preparation of aryl tellurocyanates by reaction of aryltellurenyl halides with silver cyanide [Thibaut *et al*,1978]. An alternative route to aryltellurocyanates was based on a carbon-tellurium bond cleavage of 3-oxo-2,2-dihydro-benzotellurophene by aqueous hydrogen cyanide [Talbot *et al*, 1973].

Spencer *et al* succeeded in preparing a stable DMSO solution of potassium and sodium tellurocyanate which have been used to prepare first stable alkyltellurocyanate, in a good yield [Spencer *et al*,1977].

Suzuki *et al* [Suzuki *et al*,1981] were prepared 2-carbethoxybenzyl tellurocyanate from the reaction of KTeCN with 2-carbethoxybenzyl bromide in 85% yield.

Recently, Al-Rubaie *et at* [Al-Rubaie *et al,*2003] synthesized α-tellurocyanatoketone by the reaction of KTeCN with appropriate α-bromo ketone in dry DMSO solution. The reaction of 2-amino benzyl iodide with KTeCN gave 1,4-dihydro-2-imino-3-telluraquinoline as a novel heterocyclic tellurium compounds containing nitrogen [Al-Rubaie *et al,*1997] Furthermore, the reaction of α-bromo benzaldehyde arylhydrazone with potassium tellurocyanate gave a new heterocyclic telluride [Al-Rubaie *et al,*1997]. Recently, potassium tellurocyanate was used as a cyclizing agent to prepare cyclic- tellurides. Thus, reaction of 1,2-bis-bromomethylbenzene with KTeCN gave cyclic telluride [Al-Rubaie *et al,*1996] (C_8H_8Te) in 58 % yield, along with insoluble polymeric materials $–(\text{-Te-}C_8H_8\text{-Te-})_n$ [Al-Rubaie *et al,*1996]. Additionally 2,7-dihydro-1-H-dinaphtho tellurepin was also prepared by the reaction of KTeCN with 2,2–bis(bromoethyl)biphenyl [Al-Rubaie *et al,*2004].

The corresponding reaction of potassium tellurocyanate with alcohol halide was not previously been reported. It was, therefore, of interest for us to see whether 2-chloroethanol undergo a similar cyclization reaction with potassium tellurocyante.

EXPERIMENTAL

a) *Physical measurements*

The IR spectra were recorded in the range 4000-200 cm^{-1} on a Pye-Unicam SP3-300 spectrometer using KBr discs. ^1H and ^{13}C NMR spectra were measured on a Brucker at 300 MHz, with TMS as internal reference. Microanalysis for carbon, hydrogen and nitrogen were carried out by a Perkin-Elmer 240B Elemental Analyzer. Melting points were measured by a Philip Harris melting point apparatus and uncorrected.

b) Synthesis

Preparation of potassium tellurocyanate

A mixture of finely ground Te (1.91 g;15 mmol) and dry KCN (0.97 g;15 mmol) in dry DMSO (25 ml) was heated at 100 ^{0}C for 1h under argon gas until nearly all tellurium was dissolved. To this solution added 15 ml of dry DMSO and cooled to room temperature. [Suzuki *et al*,1981], [Vogel, 1974]

Reaction of chloroethanol with potassium tellurocyanate (1)

A solution of 2-chloroethanol (1.2 g;15 mmol) was added to KTeCN solution under gentle reflux for 4h, filtered and cooled to room temperature. To the cooled mixture added (600 ml) of distilled water. The resulting mixture was extracted with ether (3×50 ml) and dried over $MgSO_4$. The mixture was distilled off to give a pale yellow precipitate. Recrystallization from ether/hexane (3/2) gave a white crystalline compound **1,** (1,3-oxatellura-2-imine) in 78% yield , m.p. 123-125 ^{0}C .

Synthesis of 3,3-dichloro-1,3-oxatellura-2-imine (2)

To a solution of compound **1** (1 g; 5 mmol) in 20 ml of dry ether was added dropwise thionyl chloride with stirring at room temperature. Removing of the solvent by using vacuum evaporater gave a white solid product. Recrystallization from ethanol afforded white crystals of compound **2** in 76% yield, m.p. 140-141 ^{0}C.

Synthesis of 3,3-dibromo-1,3-oxatellura-2-imine (3)

1,3-oxatellura-2-imine **1** (1 g ; 5 mmol) dissolved in 20 ml dry ether and a solution of bromine (0.83 ml; 5 mmol) was slowly added with stirring. A yellow precipitate was formed. Recrystallization from ethanol give 3,3-dibromo-1,3-oxatellura-2-imine **3** as yellow crystals in 63% yield, m.p. 146-147 ^{0}C.

Synthesis of 3,3-diiodo-1,3-oxatellura-2-imine (4)

Iodine (1.27 g; 5 mmol) in 20 ml dry ether was added dropwise to a solution of compound **1** (1 g; 5 mmol) in 20 ml dry ether with stirring at room temperature.

A brown precipitate gradually formed and after 3h, was collected by filtration and recrystallized from ethanol to give 3,3-diiodo-1,3-oxatellura-2-imine **4** as yellow-brown crystals in 68% yield, m.p. 134-136 ^{0}C.

Synthesis of 3-iodo-3-methyl-1 ,3-oxatellura-2-imine (5)

1,3-oxatellura-2-imine **1** (1 g ; 5 mmol) dissolved in 20 ml dry ether and a solution of methyl iodide (0.71g; 5 mmol) was added with stirring for 3 h at room temperature, a light yellow solid formed which was filtered, dried and recrystallized with ethanol to give compound **5** in 67% yield, m.p. 117-119 ^{0}C.

Synthesis of 3-ethyl-3-iodo-1 ,3-oxatellura-2-imine (6)

An excess of freshly distilled ethyl iodide (2 ml) was added slowly with stirring at room temperature to solution of **1** (0.2 g; 1 mmol) in 10 ml dry ether. After stirring for 4 h at room temperature, a yellow solid was formed. Recrystallization from ethanol to give compound 3 as yellow crystals in 70% yield, m.p. 132-134 ^{0}C.

Synthesis of 3-bromo-3-methyl-1 ,3-oxatellura-2-imine (7)

1,3-oxatellura-2-imine **1** (1 g ; 5 mmol) dissolved in 20 ml dry ether and a solution of methyl bromide (0.48g; 5 mmol) was added with stirring for 3 h at room temperature, a pale yellow solid formed which was filtered, dried and recrystallized with ethanol to give compound **7** in 70% yield, m.p. 152-154 ^{0}C.

Hydrolysis of 1,3-oxatellura-2-imine

Synthesis of 1,3-oxatellura-2-one (8)

Hydrochloric acid (5 ml;2 M) was added dropwise to a solution of compound **1** (1 g; 5 mmol) in 20 ml dry ether with stirring at room temperature.

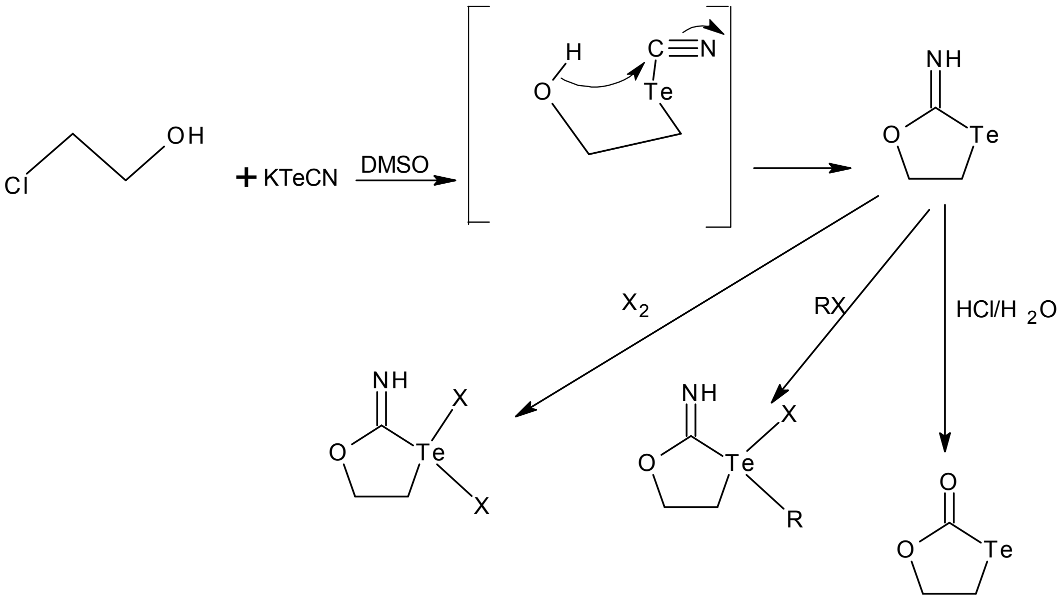
A white precipitate gradually formed which after 3 h, was collected by filtration and recrystallized from ethanol gave 1,3-oxatellura-2-one **8** as white crystals in 77% yield, m.p. 126-128 ^{0}C.

DISCUSSION

We expected that the reaction of 2-chloroethanol with potassium tellurocyanate would lead to the corresponding 2-hydroxyethyl tellurocyanate ,but instead we obtained the novel heterocycle namely 1,3-oxatellura-2-imine.

The reaction may have first afforded the organic tellurocyanate intermediate, which then cyclized spontaneously to the new cyclic telluride, (Scheme 1).

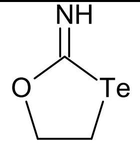
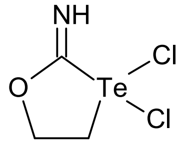
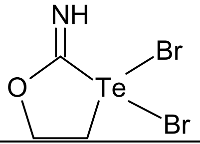
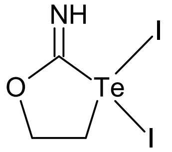
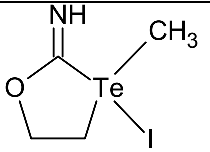
Isolated yields, melting points and analytical data for the synthesized compounds listed in Table 1. These compounds are generally brown to yellow solids except for **2** and **8.** The important IR frequencies of all compounds except **8** revealed weak bands at *ca* 3355-3348 cm^{-1} which are attributed to the stretching vibration of N-H groups ,which compound **8** showed strong band of *v*(C=O) at 1762 cm^{-1}, (Table 2). The (Te-C) aliphatic vibrations in the IR spectra for all compounds (**1-8**) are consistent with those reported previously for alkyl tellurium compounds [Al-Rubaie *et al*, 2009].



^{1}H NMR spectra of all compounds excepted **8** showed a signal due to NH protons at *ca* 9.30-9.41 ppm which absent in compound **8**,Table 2.

^{13}C NMR spectra of compounds **1-7** showed signals at *ca* (160-158) ppm due to C=N groups, while compound **8** showed signal at 176.2 ppm due to C=O, Table 2.

Table 1: Some physical properties and elemental analysis of 1, 3-oxatellura-2-imine.

Comp. No.	Formula	Colure/State	m.p. ^{0}C	%yield	Found/(calculated)(		
					C	H	N
1.		White/crystals	123-125	78	18.47 (18.12)	2.85 (2.51)	7.47 (7.04)
2.		White/crystals	140-141	76	13.78 (13.40)	2.06 (1.86)	5.27 (5.21)
3.		Yellow/crystals	146-147	63	10.41 (10.04)	1.78 (1.39)	4.11 (3.90)
4.		Yellow-brown/ crystals	134-136	68	8.19 (7.95)	1.33 (1.10)	3.35 (3.09)
5.		Yellow/crystals	117-119	67	10.89 (10.57)	1.65 (1.46)	4.63 (4.11)

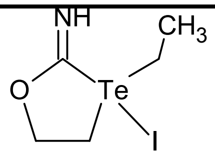
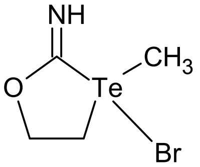
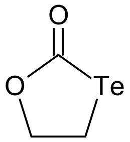
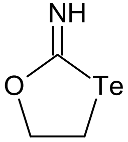
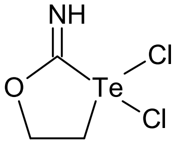
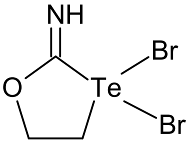
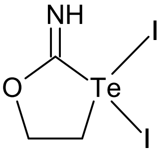
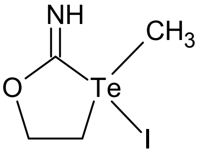
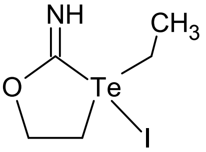
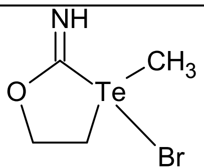
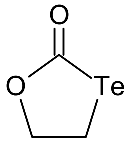
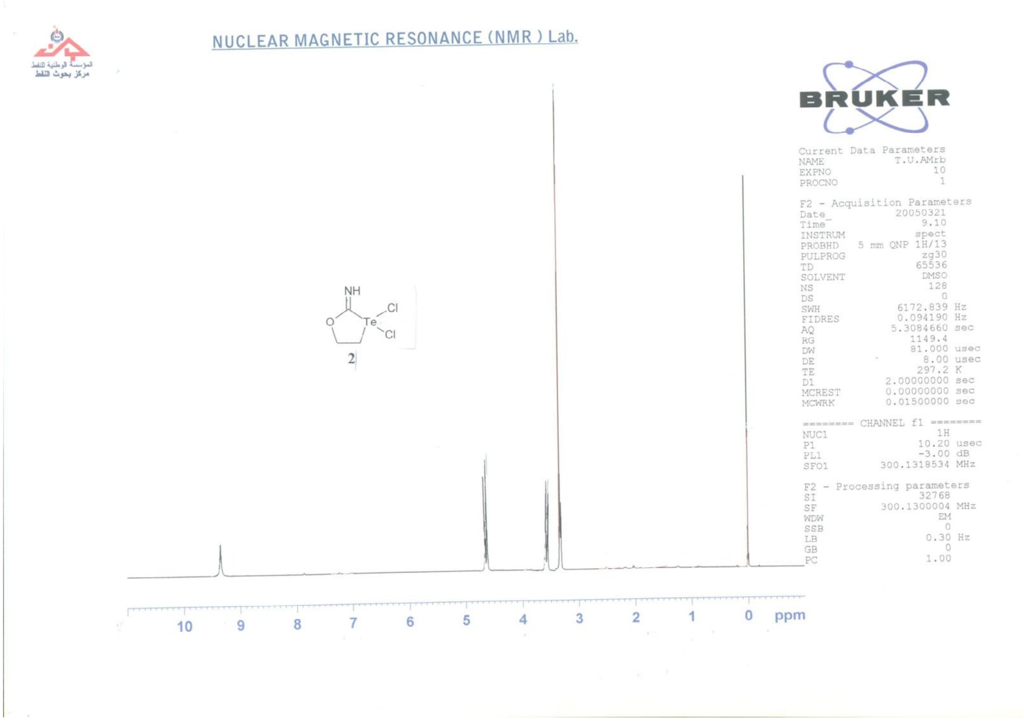
6.		Yellow/crystals	132-134	70	10.42 (10.15)	4.69 (4.41)	3.87 (3.44)
7.		Pale-Yellow/ crystals	152-154	65	17.26 (16.96)	2.78 (2.47)	5.27 (4.94)
8.		White/crystals	126-128	77	17.92 (18.03)	2.69 (2.50)	7.37 (7.01)

Table 2: IR , ^{1}H NMR and ^{13}C NMR spectra of 1,3-oxatellura-2-imine and their derivatives.

Comp. No.	Formula	)cm^{-1} (IR	^{1}H NMR(ppm)	^{13}C NMR (ppm)
1.		3355w (N-H) ; 1670s (C=N); 530w (Te-R); 1210s (C-O)	4.52(Te-CH$_2$,t,2H); 3.43(O-CH$_2$,t,2H); 9.40(NH,s,1H)	15.2 (C-Te); 60.1 (C-O); 158 (C=N)
2.		3350w (N-H) ; 1665s (C=N); 538w (Te-R); 1200s (C-O)	4.70(Te-CH$_2$,t,2H); 3.34(O-CH$_2$,t,2H); 9.32(NH,s,1H)	50.1 (C-Te); 60.3 (C-O); 160 (C=N)
3.		3352w (N-H) ; 1668s (C=N); 535w (Te-R); 1215s (C-O)	4.68(Te-CH$_2$,t,2H); 3.58(O-CH$_2$,t,2H); 9.33(NH,s,1H)	52.0 (C-Te); 60.3 (C-O); 160 (C=N)
4.		3350w (N-H) ; 1667s (C=N); 535w (Te-R); 1230s (C-O)	4.70(Te-CH$_2$,t,2H); 3.35(O-CH$_2$,t,2H); 9.30(NH,s,1H)	51.1 (C-Te); 60.0(C-O); 159 (C=N)
5.		3354w (N-H) ; 1672s (C=N); 540w (Te-R); 1210s (C-O)	2.50(CH$_3$,t,3H); 4.62 Te-CH$_2$,t,2H); 3.30 (O-CH$_2$,t,2H); 9.41 (NH,s,1H)	50.4 (C-Te); 60.1 (C-O); 160 (C=N)
6.		3351w (N-H) ; 1670s (C=N); 537w (Te-R); 1235s (C-O)	1.21(CH$_3$,t,3H); 2.08 (CH$_2$,q,2H); 4.50 Te-CH$_2$,t,2H); 3.35 (O-CH$_2$,t,2H); 9.41 (NH,s,1H)	50.2(C-Te); 60.1 (C-O); 160 (C=N)
7.		3348w (N-H) ; 1672s (C=N); 540w (Te-R); 1220s (C-O)	2.40(CH$_3$,t,3H); 4.54 (Te-CH$_2$,t,2H); 3.34 (O-CH$_2$,t,2H); 9.40 (NH,s,1H)	50.5 (C-Te); 60.1 (C-O); 158 (C=N)

8.		1740s (C=O); 535w (Te-R); 1215s (C-O)	4.61(Te-CH_2, t,2H); 3.55(O-CH_2,t,2H)	18.2 (C-Te); 62.1 (C-O); 176.2 (C=O)



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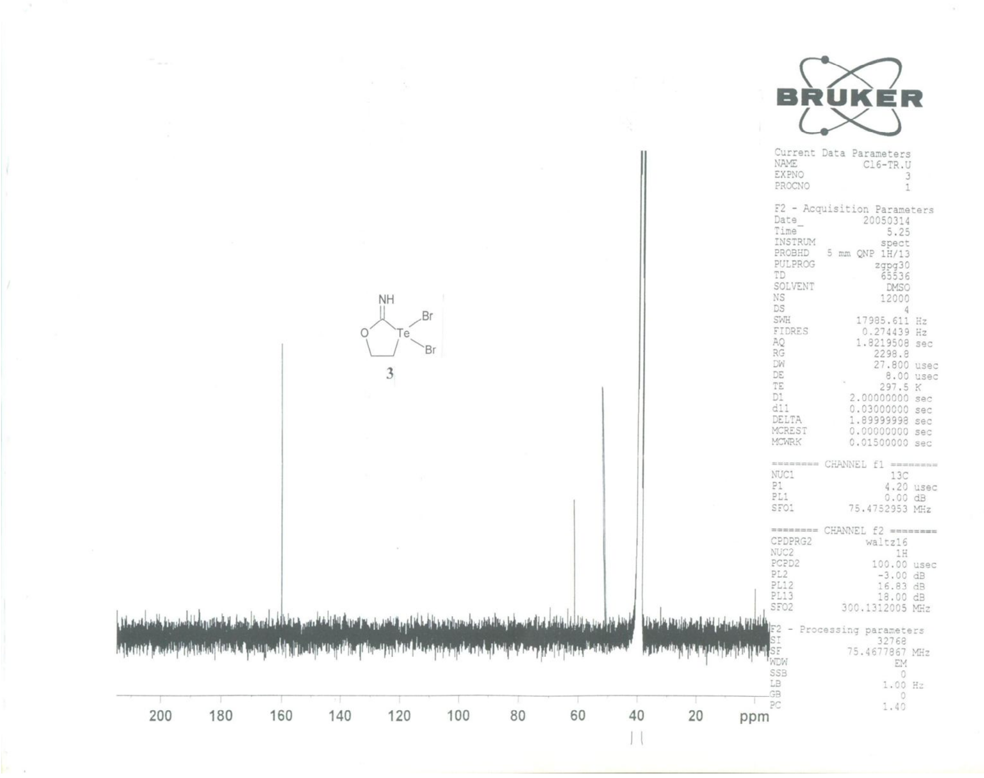
^{1}H NMR spectrum of 3,3-dichloro-1,3-oxatellura-2-imine (**2**)



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PC                    1.40
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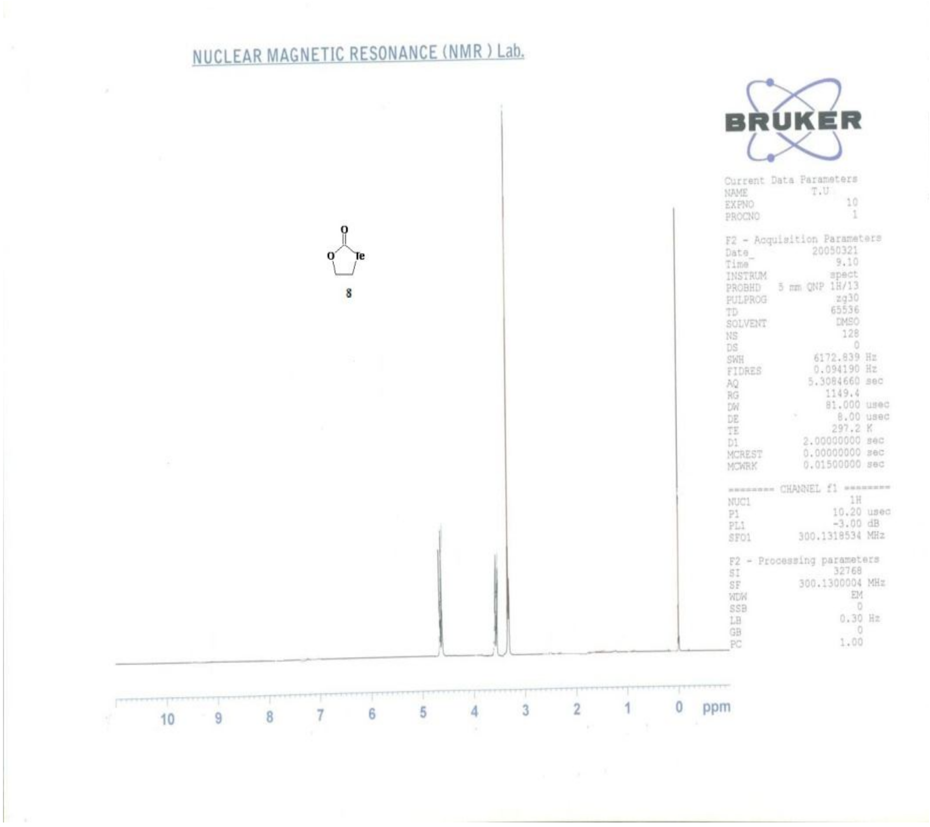
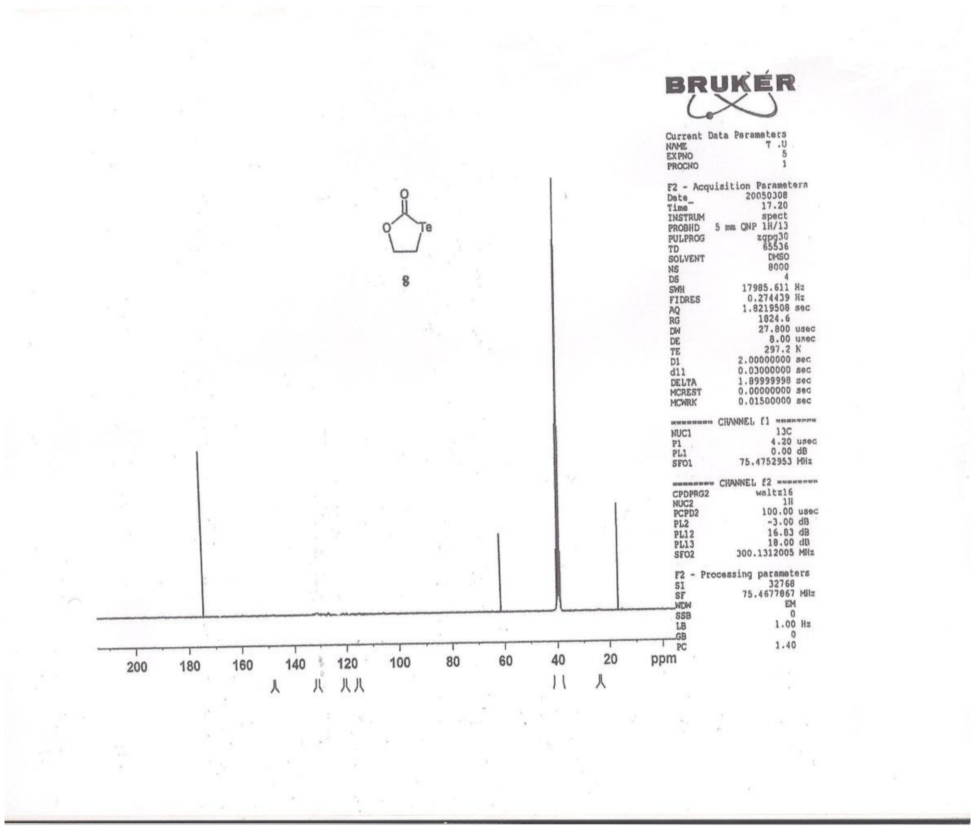
^{13}C NMR spectrum of 3,3-dibromo-1,3-oxatellura-2-imine(**3**



^{1}H NMR spectrum of 1,3-oxatellura-2-one (**8**)



^{13}C NMR spectrum of 1,3-oxatellura-2-one (**8**)

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تفاعل البوتاسيوم تلوروسيانيت مع 2-كلوروايثانول

الخلاصة

أعطى تفاعل 2-كلوروايثانول مع البوتاسيوم تلوروسيانيت مركبات حلقية غير المتجانسة جديدة تسمى 1و3-اوكساتلورا-2-ايمين **1** وبحصيلة انتاجية جيدة . الهلجنة لمركب التلورايد العضوي **1** مع الثايونيل كلوريد والبروم واليود اعطت مركبات ثنائي كلورو، وثنائي برومو, وثنائي يودو تلوريد عضوي . ان معاملة المركب **1** مع بعض هاليدات الالكيل قد ادت الى انتاج مركبات التلوريوم العضوية الجديدة . التحلل المائي للمركب **1** ادى الى تكون مركب حلق التلورايد الجديد. تم تحليل جميع المركبات باستخدام التقنية الطيفية بالتشخيص واستخدمت التحليل العنصري الدقيق واطياف الرنين المغناطيسي للبروتون والكاربون 13.