

## PREPARATION OF SOME NEW ORGANOTELLURIUM COMPOUNDS DERIVED FROM 4,4-DIHYDROXY AZOBENZENE

Assistant Professor Thana Y. Yousif  
Assistant Professor Ala I. Ayoub

*Dept. of New and Renewable Energy, College of Science /University of Mosul, Mosul-Iraq*

Received: 2/4/2020 ; Accepted: 14/6/2020

### Abstract :

A new series of organotellurium compounds derived from 4,4-dihydroxy azobenzen have been prepared by the reaction of 3-HgC1-4-OH-C<sub>6</sub>H<sub>3</sub>N=NC<sub>6</sub>H<sub>4</sub>-OH (A) with TeBr<sub>4</sub> and P-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>TeBr<sub>3</sub> to give (3-(P-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>TeBr<sub>2</sub>)-4-OHC<sub>6</sub>H<sub>3</sub>-N=N-C<sub>6</sub>H<sub>4</sub>-OH) (B̄) and (3-TeBr<sub>3</sub>-4-OHC<sub>6</sub>H<sub>3</sub>N=NCH<sub>4</sub>-OH) (B) respectively, reduction of B by sodium sulphide gave the corresponding organotellurenyl compound (C), (3-TeBr-4-OH-CH<sub>3</sub>N=N-C<sub>6</sub>H<sub>4</sub>-OH). Compound (D) (OH-C<sub>6</sub>H<sub>4</sub>-N=N-CH<sub>3</sub>-4-OH-3Te)<sub>2</sub> has been prepared by reduction of compound B or C by hydrazine hydrate. Reduction of B̄ gave the corresponding telluride 3-(P-CH<sub>3</sub>OCH<sub>4</sub>Te)-4-OH-CH<sub>3</sub>N=N-C<sub>6</sub>H<sub>4</sub>-4-OH (E). All compounds have been characterized, by IR and <sup>1</sup>H NMR spectral data and melting point was determined. The molar conductivities of the halogenated compounds (B, B̄,C) in DMSO and DMF show some weak electrolytic behavior.

**Key words:** Organotellurium, Dihydroxy azobenzen.

## تحضير بعض مركبات التلوريوم العضوية الجديدة المشتقة من ٤,٤-ثنائي هيدروكسي ازوبنزين □

□ أم علاء إسماعيل أيوب ..... أم ثناء يعقوب يوسف

جامعة الموصل/ كلية العلوم/ قسم الطاقات الجديدة والمتجددة  
موصل - العراق

### الخلاصة :

حضرت سلسلة جديدة من مركبات التلوريوم العضوية المشتقة من ٤,٤-ثنائي هيدروكسي آزوبنزين وذلك من مفاعله المركب (A)  $3\text{-HgCl-4-OH-C}_6\text{H}_3\text{N=NC}_6\text{H}_4\text{-}$  مع  $\text{TeBr}_4$  و  $\text{P-CH}_3\text{OC}_6\text{H}_4\text{TeBr}_3$  معطياً المركبين (B)  $3\text{-P-}$  و (B)  $3\text{-TeBr}_3\text{-4-}$  و  $\text{CH}_3\text{OC}_6\text{H}_4\text{TeBr}_2\text{-4-OHC}_6\text{H}_3\text{-N=N-C}_6\text{H}_4\text{-OH}$  (B) أدى اختزال المركب (B) بواسطة كبريتيد الصوديوم إلى تكوين المركب (C)  $3\text{-TeBr-4-OH-CH}_3\text{N=N-C}_6\text{H}_4\text{-OH}$ . كما حضر المركب (D)  $\text{OH-(D)}$   $\text{C}_6\text{H}_4\text{-N=N-C}_6\text{H}_3\text{-4-OH-3Te}$  من اختزال المركب B أو C بواسطة الهيدرازين المائي. إن اختزال المركب B أدى إلى تكوين التلوريد (E)  $3\text{-P-CH}_3\text{OCH}_4\text{Te-4-OH-}$   $\text{CH}_3\text{N=N-C}_6\text{H}_4\text{-4-OH}$ . شخّصت جميع المركبات المحضرة بواسطة أطياف الأشعة تحت الحمراء وأطياف الرنين النووي المغناطيسي للبروتون، وقياس درجة الانصهار (m.p.). دلت الدراسة التوصيلية المولارية للمركبات الهالوجينية الجديدة (C, B, B) في مذيب DMSO و DMF على أنها كتروليتات ضعيفة في كلا المذيبين.

الكلمات الدالة : التلوريوم العضوية، ثنائي هيدروكسي آزوبنزين .

**Introduction:**

The chemistry of organotellurium compounds has been a considerable attention in the synthesis study mainly compounds containing a carbonyl<sup>[1]</sup>, Azo<sup>[2,3]</sup>, azomethine<sup>[4,5]</sup> acetamido<sup>[6]</sup>, Quinoline<sup>[7]</sup>, heterocycles (O-, N-, and S-containing)<sup>[8]</sup>, Elemental Chalcogens<sup>[9]</sup>, chalcogen-oxygen bonds in organic synthesis<sup>[10]</sup> or amino<sup>[11]</sup> group in ortho position with respect to tellurium atom.  $\beta$ -aminoselenides and  $\beta$ -aminotellurides compounds have a potent antioxidant activity and activate the carbonic anhydrase may have applications for memory therapy and carbonic anhydrase deficiency syndromes<sup>[12]</sup>.

Generally, aromatic system having tellurium group attached to amino group are difficult to synthesis<sup>[13,14,15]</sup>.

The present work described the synthesis of some new compounds derived from 4,4'-dihydroxyazobenzene containing an OH-group ortho position to tellurium. Furthermore such hydroxyl compounds might play an important role in polymerization of di-OH with the formaldehyde.

**Experimental:****a) Physical measurement:**

<sup>1</sup>H NMR spectra were run in DMSO-d<sub>6</sub> at 60 MHz on a Hitachi perkin Elmer R-248. Infrared were recorded on Beckman TM spectrophotometer with KBr discs.

The conductivity measurements were done for 10<sup>-3</sup> M solution of some compounds at ambient temperature using WTW, LBR instrument with of 0.0577 cm<sup>-1</sup> cell constant.

**b) Synthesis:**

Some compounds were prepared under nitrogen atmosphere.

**4,4'-Dihydroxyazobenzene mercury chloride (A)<sup>[16]</sup>**

A mixture of 4,4'-Dihydroxyazobenzene (4mmol) and mercuric acetate (1 mmol) in ethanol was refluxed for 4 hrs, followed by the addition of equimolar quantity of lithium chloride causes the formation of yellow precipitate. The compound was purified by recrystallized from ethanol to give fine yellow crystals.

**4,4'-Dihydroxyazobenzene tellurium tribromide (B).**

A solution of compound A (0.01 mmol) and tellurium tetrabromide (0.01 mmol) in dioxane was refluxed for 4 hrs. The orange solution converted to violet, the mixture was cooled and the white plate of complex of mercuric halide and the dioxane was filtered. The solvent was evaporated and the solid precipitate was recrystallized from ethanol to give violet crystals.

**4,4'-Dihydroxyazobenzene -3-(*P*-methoxy phenyl tellurium dibromide) ( $\bar{B}$ ).**

This was prepared by refluxing equimolar quantities of compound A (0.01 mmol) with Methoxyphenyl-tellurium tribromide (0.01 mmol) in dry dioxane under continuous stirring for (4hrs) similar procedure to that for compound (B) was followed to give violet crystals of the product.

**Compound C (3-TeBr-4-OH-C<sub>6</sub>H<sub>3</sub>N=N-C<sub>6</sub>H<sub>4</sub>-OH)** and **compound E (3-(P-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)-Te-4-OH C<sub>6</sub>H<sub>3</sub> N=N-C<sub>6</sub>H<sub>4</sub>-OH)** were prepared by the following general method.

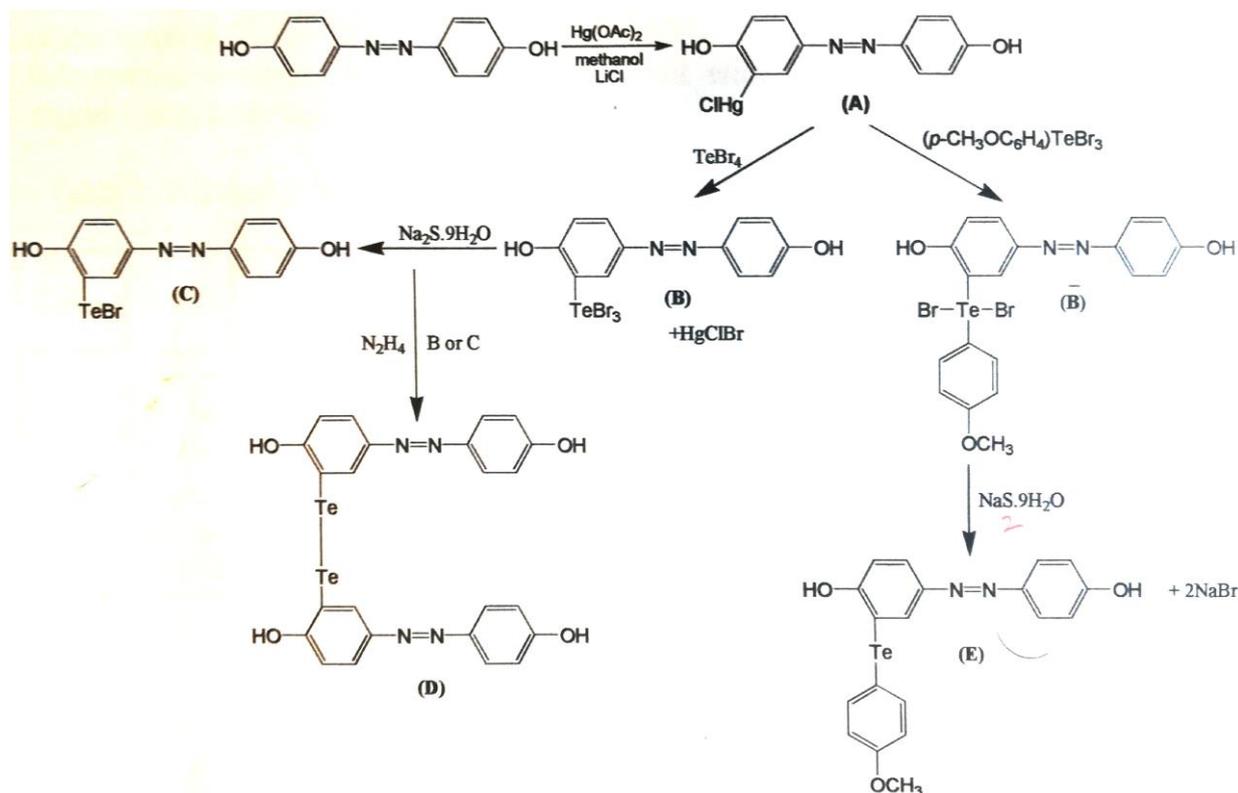
An excess of Na<sub>2</sub>S.9H<sub>2</sub>O was added to hot solution of compounds B (0.01 mmol) or B (0.01 mmol) in water. The mixture was cooled to 25°C and the solid was formed, filtered off and recrystallization from ethanol to give pure yellow compounds in both cases: compound B gives product C and B give product E.

#### **Bis (4,4-Dihydroxyazobenzene) ditelluride.**

Compound B (0.01 mmol) or C (0.01 mmol) was dissolved in 30 ml ethanol was heated the hydrazine hydrate in ethanol was added drop under continuous heating and stirring. A vigorous reaction was derived, the addition continued until the evolution of nitrogen gas was ceased. The mixture was cooled to 20°C to afford orange crystals.

#### **Results and discussion:**

The symmetrical structure of azobenzene lead to ortho-mercurated compound on its reaction with mercuric acetate at any of the two phenyl groups with no competition<sup>[15,17,18]</sup>. In the present work the addition of OH groups at para position of two phenyl group of azobenzene regioselectively enhances the mercuration of 4,4-Dihydroxyazobenzene. However OH is a strong ortho-and para directing group in the absence of an acid<sup>[19]</sup> and reaction of mercuric acetate with 4,4-dihydroxyazobenzene at position-3 according to *Scheme 1*.



Scheme 1: The reaction pathway of preparing compounds (A-E).

Compound A which represents a superior starting material for the new organotellurium compounds (B-E) (*Scheme 1*) was precipitated as a yellow product.

Reaction of A with  $\text{TeBr}_4$  and  $p\text{-CH}_3\text{OC}_6\text{H}_4\text{TeBr}_3$  gave compounds B and B' respectively (*Scheme 1*). Reduction of B' with  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  gave the unexpected unsymmetrical telluride (E) while reduction of organotellurenyl tribromide (B) by the same reducing agent leads to the formation of organotellurenyl bromide (C). On the other hand reduction of compound C or B with hydrazine leads to the formation of the expected ditelluride (D).

The physical properties of these new compounds (A-E) are listed in *Table 1*. The IR spectral data of all compounds show an absorption band at  $\text{Ca } 3250\text{-}3400\text{cm}^{-1}$  attributed to (O-H). And another two bands appeared in the region  $1330\text{-}1450$  and  $1225\text{-}1240\text{cm}^{-1}$  assigned to (N=N) and (N-C) respectively.

$^1\text{H}$  NMR spectra recorded in DMSO- $d_6$  revealed the presence of single signal with chemical shift of  $\text{Ca. } (11.9\text{-}12.6 \text{ ppm})$  attributed to OH group and multiplied signal at  $\text{Ca. } (7.1\text{-}7.86 \text{ ppm})$  attributed to the resonance of phenyl proton and single signal at 3.8 for  $\text{OCH}_3$  for compounds B, E (*Table 1*).

The conductivity data (*Table 1*) show, in DMSO and DMF that the halogenated compounds dissociate as 1/1 electrolytes plots of  $\Lambda_M$  against (concentration)" are linear over the range  $10^{-3}\text{-}10^{-4}\text{M}$ . The molar conductance of halogenated compounds is in good agreement with previously reported data for organotellurium compounds<sup>[20,21]</sup>.

**Table 1: Physical properties of compound A and tellurium compounds.**

Comp	Color	m.p (°C)	IR Data (cm <sup>-1</sup> )			<sup>1</sup> H NMR (ppm)			Conductivity cm <sup>2</sup> .ohm <sup>-1</sup> .mol <sup>-1</sup>	
			<i>v</i> (N=N)	<i>v</i> (N-C)	<i>v</i> (O-H)	OH	Ar-H	OC H <sub>3</sub>	DMSO	DMF
A	Yellow	160	1430	1240	3260-3325	12.6	7.1-7.78	---	---	---
B	Violet	185	1440	1235	3200-3300	11.9	7.1-7.86	---	58	100
C	Yellow	100	1435	1230	3250-3300	12.5	7.1-7.75	---	45	85
D	Orange	115	1455	1230	3200-3300	12.6	7.1-7.81	---	---	---
B̄	Violet	151	1445	1440	3250-3350	11.9	7.1-7.61	3.8	40	95
E	Yellow	108	1435	1325	3200-3350	12.5	7.1-7.81	3.8	---	---

### Acknowledgment:

The authors are thankful to the university of Basrah, College of Science for providing laboratory facilities, Thanks are also to Prof. A. Z. Al-Rubaie.

### References:

1. M.R. Detty, B.J. Murray, D.L. Smith and N. Zumbulyadis. *J. Am. Chem. Soc.* 195. 875 (1983).
2. M.A.K. Ahmed, W.R. McWhinnie and T.A. Hamor. *J. Organomet. Chem.* 281,205(1985).
3. W. A. Al-Masoudi, R. H. Al-Asadi, R. M. Othman and N. A. Al-Masoudi. *European J. Chem.*, 6(4), 374-380(2015).
4. N. Al-Salim, T.A. Hamor and W.R. McWhinnie. *J. Organomet. Chem.* 293. 219(1985).
5. V.I. Minkin, A.A. Maksimenko, O.K. Mehrota, A.G. Maslakov, and D.S. Yufit, *J. Organomet. Chem.* 248. 36(1988).
6. T. Junk and K.J. Irgolic. *Phosph. And sulfur.* 38. 121(1988).
7. A.A. Al-Fregi, H. A. Jaid and H. T. Abdulsahib. *European J. Chem.*, 8(3), 218-223(2017).
8. D. Tanini and A. Capperucci. *New J. Chem.*, 43, 11451-11468(2019).
9. V. A. Potapov and S. V. Amosova. *Russian J. Org. Chem.* 39(10), 1373-1380(2003).
10. P. Alexandra, S. Cristian and S. Anca. *Physical Sciences Rev*, 4, 5(2018).
11. S.A. Al-Jadan. M.Sc. Thesis, University of Basrah (1990).
12. D.T. Antonella, C.C. T. Supuran and A. Angelib. *Bioorg. Med. Chem.* 27 (2), 410-415(2019).
13. A) A.K. Singh, V. Srivastava and B.L. Khandelwal. *Polyhedron.* 9.495(1990).  
B) B.L. Khandelwal. The 6th international conference on the chemistry of selenium and Tellurium, Osaka, Japan, Abstract P. 18, 1991.
14. H.B. Singh, N. Sudha, A.A. West and T.A. Hamor, *J. Chem. Soc. Dalton Tran*, 907 (1990).

15. P. V. Roling, J.L. Dill and M.D. Rausch. *J. Organomet. Chem.* 69, C3 (1974).
16. A.Z. Al-Rubaie. N.I. Al-Salim, S.A. Al-Jadaan. *J. Organomet. Chem.*, 448, 67(1993).
17. P.V. Roling, *J. Org. Chem.*, 22. 2421(1975).
18. M.A.K. Ahmed. E.A. Me Carthy and W.R. McWhinnie, *J. Chem. SOC. Dalton Trans.*, 771(1986).
19. J. March. "Advanced organic chemistry". 3rd Edn., J. Wiley and Sons, New York, (1985).
20. A.Z. Al-Rubaie, H. A-Shirayada and A.I. Aroob, *J. Organomet. Che.*, 356, 49(1988).
21. A.Z. Al-Rubaie, A.A. Al-Najar and F.A. Jassim, *Inorg. Chem. Acta* 175, 181(1990).