

Synthesis and Configurational Studies of Some 2-Methyl-1-Telluracyclohexane Derivatives

ALA'A I. AYOOB†, TALAL A. K. AL-ALLAF* and SALIM A. MOHAMMED

Chemistry Department, College of Science
University of Mosul, Mosul, Iraq

New heterocyclic tellurium compounds of the general formula $(2\text{-CH}_3\text{-C}_5\text{H}_9\text{-1-Te(RX))$, $\text{R}=\text{X}=\text{Cl, Br, I}$ or $\text{R}=\text{methyl, ethyl, allyl}$; $\text{X}=\text{Cl, I}$ or $\text{R}=\text{ethyl, allyl, benzyl}$; $\text{X}=\text{Br}$ or $\text{R}=\text{methyl, phenyl}$; $\text{X}=\text{BPh}_3$, have been prepared and characterized on the basis of their IR and ^1H NMR spectral data. It was shown by NMR that both *cis*- and *trans*-geometrical isomers for some of these compounds are present in solution. Also all the compounds prepared showed considerable stability towards reductive-elimination reactions and do not interact with the solvent used. The molar conductivities of these compounds in DMSO and DMF indicate that there is some ion pairing.

INTRODUCTION

It was recently shown by Al-Rubaie and co-workers¹ that the compounds 2-methyl-1-organo-1-telluracyclopentane present as a mixture of *cis*- and *trans*- isomers with *trans*-isomer as a major product and the isomer ratio was found to depend markedly on the size of the alkyl group attached covalently to the tellurium atom. Structural assignments by X-ray diffraction for the compound $\text{C}_8\text{H}_8\text{Te(RX)}$ ² showed that the ring is planar with alkyl-Te in *trans*-relationship to the halogen present in the distorted octahedral structure. In order to examine the properties of organotellurium compounds having six-membered ring, we decided to prepare the compounds $(2\text{-CH}_3\text{-C}_5\text{H}_9\text{-1-Te(RX))$, with various *R* and *X* groups and to study their behaviours by IR, ^1H NMR spectroscopy and their molar conductivities in DMSO and DMF.

EXPERIMENTAL

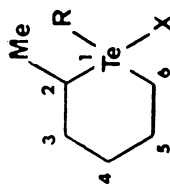
^1H NMR spectra were recorded on a Hitachi Perkin-Elmer R-248 HR-60MHz spectrometer using the deuterium signal of the solvent (DMSO- d_6) as a field lock signal. IR spectra were recorded on a Beckman TM spectrometer with KBr discs in the range 200-4000 cm^{-1} . Solution conductivities were measured with a WTW conductivity meter LBR, using a standard conductivity cell with cell constant of 0.0577.

Preparation of the Compounds: 2-Methyl-1, 1-dihalo-1-telluracyclohexane

These compounds (Ia, IIa and IIIa/ Table 1) were prepared according

*Chemistry Department, College of Science, University of Basrah, Basrah, Iraq.

TABLE I
PHYSICAL PROPERTIES OF TELLURIUM COMPOUNDS



| Compound | X | R | m.p. (°C) | IR data cm ⁻¹ | | | Conductivity (Λ _m) ^a (ohm ⁻¹ cm ² mol ⁻¹) | | |
|----------|------------------|---|--------------|--------------------------|------------------|-----------|---|------|------|
| | | | | ν C-H (stret.) | ν C-H (bend.) | ν Te-C(R) | DMSO | DMF | |
| Ia | Cl | Cl | 165-167 | † | 1390 | 515 | 475 | 8.5 | 10.1 |
| Ib | Cl | CH ₃ | 163-175 | 2870 | 1320 | 525 | 470 | 28.7 | 56.7 |
| IIa | Br | Br | 155-157 | 2870 | 1380 | 510 | 485 | 15.1 | 20.1 |
| IIb | Br | C ₂ H ₅ | 125-128 | 2880 | 1325 | 515 | 470 | 25.7 | 46.3 |
| IIc | Br | C ₂ H ₅ | 165-168 | 2870 | 1455 | 510 | 485 | 29.1 | 57.1 |
| IId | Br | C ₆ H ₅ CH ₂ | 162 | 3035 | 1480 | 525 | 470 | 15.1 | 27.3 |
| IIIa | I | I | 140-143 | 2875 | 1460 | 515 | 465 | 16.1 | 18.1 |
| IIIb | I | CH ₃ | 219-221 | 2870 | 1320 | 530 | 475 | 25.5 | 48.3 |
| IIIc | I | C ₂ H ₅ | 170-174 | 2870 | 1320 | 520 | 475 | 24.3 | 42.1 |
| IIId | I | C ₂ H ₅ | 154-156 | 2890 | 1455 | 505 | 485 | 27.1 | 51.1 |
| IVa | BPh ₄ | CH ₃ | 235-237 | 3030 | 1480 | 505 | 455 | 21.1 | 43.7 |
| IVb | BPh ₄ | C ₆ H ₅ | 217 | 3035 | 1480 | 505 | 470 | 20.1 | 36.7 |

^aMolar conductivities were measured for 10⁻³ M solutions of the compounds. [(C₂H₅)₄N] Cl : Λ_m 30(DMSO) 80(DMF) ohm⁻¹ cm² mol⁻¹.
†Band not very well resolved.

to the methods described in the literature,¹⁻⁴ with some modifications with respect to the ring (cyclohexane), which is as follows:

(Ia) 2-Methyl-1,1-dichloro-1-telluracyclohexane

This was prepared by the action of thionyl chloride (SO_2Cl_2) on 2-methyl-1-telluracyclohexane in ether. The white solid thus formed was filtered off and recrystallized from ethanol to give white crystals.

(IIa) 2-Methyl-1,1-dibromo-1-telluracyclohexane

This was prepared by the treatment of bromine solution in ether with 2-methyl-1-telluracyclohexane as a white precipitate. The solid was filtered off and recrystallized from ethanol as white crystals.

(IIIa) 2-Methyl-1,1-diiodo-1-telluracyclohexane

This compound was prepared according to the following procedure: tellurium dust (0.01 mol) was added to a mixture of 1,5-dibromohexane (0.01 mol) and sodium iodide (0.08 mol) in 2-methoxy ethanol (100 ml) as a solvent. The mixture was heated slowly with stirring for *ca.* 2 hrs until the colour became deep-red. The reaction mixture was filtered through Celite while it is hot and the solution was cooled to room temperature. Distilled water (300 ml) was added to the solution and a brown precipitate was quickly formed. The solid was filtered off, washed with water, then with alcohol, and recrystallized from ethanol to give off white crystals.

(IIIb) 1, 2-Dimethyl-1-iodo-1-telluracyclohexane

This was prepared by the stepwise addition of sodium borohydride (NaBH_4) to the hot alcoholic solution of (IIIa) until the brown colour of the solution had completely disappeared. The reaction mixture was filtered through Celite, and distilled water (500 ml) was added onto the solution. The product was extracted with ether and the ethereal solution was dried over calcium chloride. To the dry ethereal solution was added an excess of freshly distilled methyl iodide, and the mixture was allowed to stand for 12 hrs. By which time a white solid started to deposit, it was filtered off and recrystallized from ethanol as white crystals.

Similarly the compounds I Ib, I Ic, I Id, I Ic and I Id were prepared from the reaction of 2-methyl-1-telluracyclohexane and the corresponding alkyl halide (Table 1).

(Ib) 1,2-Dimethyl-1-chloro-1-telluracyclohexane

This compound was prepared by refluxing an alcoholic solution of (IIIb) (0.01 mol) with a suspension of silver chloride (0.01 mol) in water for *ca.* 2 hrs. The reaction mixture was filtered while it is hot and the clear solution was cooled to room temperature. An off-white precipitate was

formed on crystallization from ethanol.

(IV) 1, 2-Dimethyl-1-telluracyclohexane tetraphenylborate

This was prepared by heating a mixture of (IIIb) (0.01 mol) and sodium tetraphenylborate (NaBPh_4) (0.01 mol) in ethanol under continuous stirring for *ca.* 2 hrs. A white solid was formed, it was filtered off and recrystallized from dimethylformamide (DMF)/water (1 : 3 ratio) to give white crystals.

(IVb) 2-Methyl-1-phenyl-1-telluracyclohexane tetraphenylborate

Similarly, this was prepared by heating a mixture of (IIIa) (0.01 mol) and NaBPh_4 (0.01 mol) in ethanol for *ca.* 2 hrs. The white solid thus formed was filtered, washed with water and ethanol, and recrystallized from DMF/ H_2O to give white crystals.

RESULTS AND DISCUSSION

The compounds Ia, b; IIa, b, c, d; IIIa, b, c, d and IVa, b were prepared as white solids, their physical properties are listed in Table 1.

The IR spectral data for these compounds showed no unusual features. The ν (Te-C(R)) bands are found between 505 and 530 cm^{-1} and the ν (Te-C2, 6) bands between 455 and 485 cm^{-1} .

The molar conductivities (A_M) for the compounds are measured in DMSO and DMF solutions (Table 1) for 10^{-3} M concentrations (C). The data obtained from the plots between A_M against \sqrt{C} showed that these compounds are weak electrolytes in both solvents. This indicates that an appreciable ion pairing between the cation (tellurium site) and the anion is existed, but in DMSO at least, the values of A_M reach those expected for 1 : 1 electrolytes.⁵⁻⁸ It is also noted that the values of A_M for the dihalide compounds (Ia, IIa and IIIa) are considerably less than those for the rest of tellurium compounds (Table 1). This may be attributed to the possible association of these compounds via weak ionic bonds in both solvents^{1,9} as well as due to the inductive effects caused by the halogens attached covalently to tellurium.⁴

The ^1H NMR spectral data for the tellurium compounds (2-Me) C_5H_9 -(Te)RX recorded in DMSO- d_6 are listed in Table 2. The previous work¹ concerning the compounds (2-Me) $\text{C}_4\text{H}_7\text{Te}(\text{RX})$ showed the presence of *cis/trans* geometrical isomers in solution and their proportions depend markedly on the size of R group used. Similarly, in the present work, we have also observed the *cis/trans* isomerizations with the compounds where $\text{R}=\text{CH}_3$ or C_2H_5 . The rest of other compounds where $\text{R}=\text{C}_3\text{H}_5$, C_6H_5 , $\text{C}_6\text{H}_5\text{CH}_2$, the *trans*-isomer being the predominant one, which could well be due to steric factors inhibited the formation of *cis*-isomer (Scheme 1).

TABLE 2
 PROTON CHEMICAL SHIFT (δ ppm)* FOR 2-methyl-1-
 TELLURACYCLOHEXANE DERIVATIVES

| Compound | Chemical shifts (ppm) and assignment† | cis/trans proportion |
|----------|--|----------------------|
| IIa | 1.8(d) C2-CH ₃ 1.65-1.55(m) H(C3, 4, 5) 2.1-2.25(m) H(C2, 6) | 0/100 |
| IIb | 1.9(d) C2-CH ₃ trans- 1.55-1.75(m) C2-CH ₃ cis+CH ₃ CH ₂ 2.55-1.6(m) H(C3, 4, 5) 3.45-2.9(m) H(C2, 6) | 20/80 |
| IIc | 1.52(d) C2-CH ₃ trans- 2.5-1.7(m) H(C3, 4, 5) 3.45-2.9(m) H(C2, 6)+Te-CH ₂ (α) 4.85-5.3(m) CH(β) 5.6-6.1(m) CH(γ) | 0/100 |
| IIId | 1.6(d) C ₂ -CH ₃ trans- 2.5-1.7(m) H(C3, 4, 5) 3.45-2.9(m) H(C2, 6) 4.35(s) CH ₂ (benzyl) 7.45(s) Ar-H | 0/100 |
| IIIa | 2.1(d) C2-CH ₃ 1.75-1.5(m) H(C3, 4, 5) 2.25-2.15(m) H(C2, 6) | 0/100 |
| IIIb | 1.5(d) C2-CH ₃ cis- 1.65(d) C2-CH ₃ trans- 2.1(s) Te-CH ₃ cis- 2.3(s) Te-CH ₃ trans- 2.8-1.9(m) H(C3, 4, 5) 3.5-2.9(m) H(C2, 6) | 30/70 |
| IIIc | 2.1(d) C2-CH ₃ 1.85-1.6(m) C2-CH ₃ +CH ₃ CH ₂ cis- 2.7-1.85(m) H(C3, 3, 5) 3.55-3.0(m) H(C2, 6) | 20/80 |
| IIId | 1.6(d) C ₂ -CH ₃ trans- 2.6-1.75(m) H(C3, 4, 5) 3.55-3.1(m) H(C2, 6)+Te-CH ₂ (α) 5.52-5.05(m) CH(β) 6.28-5.21(m) CH(γ) | 0/100 |
| IVa | 1.4(d) C2-CH ₃ cis- 1.55(d) C2-CH ₃ trans- 2.1(s) Te-CH ₃ cis- 2.2(s) Te-CH ₃ trans- 2.65-1.75(m) H(C3, 4, 5) 3.3-2.7(m) H(C2, 6) 7.5-6.65(m) Ar-H | 27/73 |

TABLE 2 (cont.)

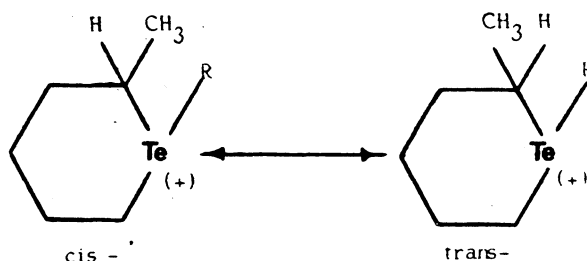
| Compound | Chemical shifts (ppm) and assignment† | | cis/trans proportion |
|----------|---------------------------------------|---------------------------|----------------------|
| IVb | 1.7(d) | C2-CH ₃ trans- | 0/100 |
| | 2.7-1.9(m) | H(C3, 4, 5) | |
| | 3.6-3.2(m) | H(C2, 6) | |
| | 8.2-6.8(m) | Ar-H | |

*Downfield from internal TMS, using DMSO-d₆ as a solvent.

†Abbreviations: *s*, *d*, *m* means singlet, doublet (with $J \cong 7$ Hz) and multiplet respectively. α , β , γ are for the allyl carbons CH₂-CH=CH₂, respectively.

Scheme 1

On the other hand, the type of tellurium ring; six (-C₅H₉Te)* or five (-C₄H₇Te)¹ membered ring had no significant effects on cis/trans isomerizations.



Scheme 1

However, the *cis*- and *trans*- assignments were carried out as follows: e.g., R=CH₃, the ¹H NMR spectrum comprises the presence of four signals for C2-CH₃ and Te-CH₃: two sets of doublets for C2-CH₃ were observed; the first set ($\delta = 1.5$ ppm) has low intensity which is for *cis*-C2-CH₃ (*cis*-isomer signals usually appeared at high field¹¹) and the second set ($\delta = 1.65$ ppm) has higher intensity which is for *trans*-C2-CH₃, and two single signals at lower field; $\delta = 2.15$ and 2.3 ppm which are for *cis*- and *trans*-Te-CH₃, respectively. The *cis*- and *trans*-proportions were calculated by measuring the area under peak (from the integration). The *cis/trans* ratio for compound IIIb (R=CH₃) is *ca.* 30/70, and this becomes *ca.* 20/80 on going to compound IIIc (R=C₂H₅) and become *ca.* 0/100 on going to compounds where R=C₃H₅ or C₆H₅ or C₆H₅CH₂, i.e., the *trans*- becomes the only isomer present in solution.

Furthermore, compound IIIb was found, by recording its ¹H NMR at every 30 min. interval, to be stable in DMSO-solution, which is no change was shown in its ¹H NMR pattern even after 24 hrs. This supports the fact that organotellurium (IV) compounds are stable enough towards

*Present work.

reductive-elimination reactions,^{6,7} also stable towards interaction with the solvent DMSO.¹⁰

REFERENCES

1. A. Z. Al-Rubaie, H. A. Al-Shirayda and A. I. Ayoob, *J. Organometal. Chem.*, **356**, 49 (1988).
2. R. H. Jones and T. A. Hamor, *J. Organometal. Chem.*, **234**, 299 (1982).
3. R. F. Ziolo and W. H. H. Gunther, *J. Organometal. Chem.*, **146**, 245 (1978).
4. N. Zumbulyadis and H. J. Gysling, *J. Organometal. Chem.*, **192**, 183 (1980).
5. F. H. Musa and W. R. McWhinnie, *J. Organometal. Chem.*, **159**, 37 (1978).
6. N. S. Dance, W. R. McWhinnie, J. Mallaki and Z. M. Mirzai, *J. Organometal. Chem.*, **198**, 131 (1980).
7. A. Z. Al-Rubai, W. R. McWhinnie, P. Granger and S. Chapelle, *J. Organometal. Chem.*, **234**, 287 (1982).
8. A. Z. Al-Rubaie, H. A. Al-Shirayda and A. I. Ayoob, *Inorg. Chim. Acta*, **134**, 139 (1987).
9. J. D. McCullough, *Inorg. Chem.*, **12**, 2669 (1973).
10. D. P. Rainville and R. A. Zingaro, *Inorg. Chim. Acta*, **86**, L33 (1984).
11. J. P. Stother, C. T. Tan and K. C. Teo, *J. Mag-Res.*, **20**, 570 (1975).

[Received: 12 August 1989; Accepted: 28 February 1990]

AJC-144

FOURTH ASIAN CHEMICAL CONGRESS

Venue : Beijing, China

During: August 26-30, 1991

Topics: Organic chemistry of natural products, Analytical chemistry and analytical instrumentation, Environmental Chemistry, Agrochemistry, Coordination Chemistry, Polymer Science, Photochemistry, Chemical education, Computer in Chemistry practice and Catalysis.

Last date for submission abstract of paper March 15, 1991

Address for Communication

Prof. Dehe Zhang

Secretary-General of 4th ACC

Chinese Chemical Society

P.O. Box-2709, Beijing-100 080, China