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A New Approach in Synthesis of Some Telluro Compounds

REKHA RANI, RAJEEVA RANJAN, ASHUTOSH KUMAR†, NAVIN SHARMA† and S. SHARMA*
Department of Chemistry, Magadh University, Bodh Gaya-824 234, India
E.mail: sharma.shivadhar@gmail.com

Aryl mercuric chloride (ArHgCl) undergoes transmetallation reaction with aryl tellurium chloride ($ArTeCl_3$) to form diaryl tellurium chloride ($Ar-TeCl_2-Ar$). This compound on further reduction forms diaryl telluroether or diaryl telluride. This compound may also be formed by the addition of tellurium powder to phenyl magnesium iodide in THF, followed by vigorous stirring. This method, however is not suitable when phenyl group bears substituent like NH_2 or NHR or NR_2 group. But the above transmetallation reaction helps to form the various diaryl telluro compounds having various substitution on aryl rings. On the basis of IR and NMR spectral study, the geometry around Te in Ar_2TeCl_2 is found to be trigonal bipyramidal with two chlorine occupying the axial positions and two aryl group occupying the two equatorial point while the only lone pair occupies one of the corners of the triangle.

Key Words: Telluroether, Transmetallation.

INTRODUCTION

Recently the synthesis of a variety of compounds containing thioether, selenoether groups with alkane backbones like $RX-(CH_2)_n-XR$, (R = Me, X = S, Se, n = 1-3) have been reported[1-4]. Various reports involving the design and synthesis of macrocyclic and macrobicyclic compounds containing several recognition sites have been made recently[5-10]. There is a good number of examples of compounds containing soft sulphur[11,12] or phosphorous[13,14] and hard nitrogen which have been studied. But to our best of knowledge neither selenium nor tellurium has been incorporated into such compounds. Some homoleptic seleno ether macrocycles, however, have been reported[15,16]. Sadekov *et al.*[17] have reported the synthesis of *bis*(2-formylphenyl)-telluride in which air sensitive reactions were carried out under an inert atmosphere. Recently a detailed account of tellurium containing compounds has been given by Hope and Levason[18] and then by Singh and Sharma[19] with FT, NMR instruments there is a good possibility of using ^{125}Te-NMR to understand the solution behaviour of tellurium bonded to other atoms. The tellurium compounds and organotellurium compounds may be used as single source precursors for MOCVD of 11-VI semiconductors has inhanced interest immensely in chemistry of tellurium. Keeping all these facts in mind we report the synthesis of some telluroethers with characterization by their infrared and NMR spectra.

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†Department of Chemistry, Z.A. Islamian College, Siwan-841 226, India.

EXPERIMENTAL

Commercially available tellurium powder, *p*-toluidine, mercuric chloride, sodium metabisulphite, hydrazine hydrate were used without further purification. Tellurium tetrachloride was prepared by standard method[20] and was stored under absolutely dry condition due to its highly hygroscopic nature. The precursor phenyl tellurium trichloride was prepared by the method reported by Paul *et al.*[21] which involved the refluxing of tellurium tetrachloride with tetraphenyltin in dry toluene for 3-4 h. 4-Methylphenyl tellurium trichloride and 4-ethylphenyl tellurium trichloride were prepared by the method reported by Irgolic and Zingars[22]. 2-Chloromercury aniline was prepared by the method reported by Makarova and Nesmeyanov[23]. Now 2-(Cl_2TeAr-R) aniline (where R = H, CH_3 or C_2H_5 at position 4') were prepared by refluxing the equimolar amounts of aryl tellurium trichloride with 2-(chloromercury) aniline in dry chloroform for nearly 6 h. The solution was cooled up to nearly room temperature and the precipitated $HgCl_2$ was filtered off. The filterate was concentrated whereby a pale yellow crystalline product separated out. It was recrystallized from benzene. Finally the diaryl dichloro telluroether was converted into diaryl telluroether by taking the aqueous suspension of diaryl dichlorotelluroether with excess of $Na_2S_2O_5$ solution and stirring the resulted solution at 50-55 ºC for 2 h whereby a dense yellow oil appeared which was separated out and was finally extracted from *n*-hexane. The percentage of C, H and N was estimated on Perkin-Elmer 240C-rapid elemental analyzer at IIT, Delhi. For the estimation of tellurium, the compounds were first decomposed by their treatment with 1:1 mixture of nitric acid and perchloric acid and then tellurium was estimated volumetrically by $K_2Cr_2O_7/(NH_4)_2SO_4$. $FeSO_4$ titration. The infrared spectra of compounds were recorded on a Nicolet 5 DXFT-IR spectrometer in KBr pellets and ^{1}H NMR spectra were recorded at 99.55 MH/on Jeol. JNMFX-100 FT-NMR spectrometer using TMS as an internal standard at IIT, Delhi.

RESULTS AND DISCUSSION

The physical properties and per cent composition of different compounds are given in Table-1. The main infrared bands with their assignment in different compounds have been given in Table-2. Compounds **1, 5, 6, 7, 8, 9** and **10** absorb at 3410-3383 and 3200-3188 cm^{-1} due to ν_{asym} and ν_{sym} of N-H vibration[21-25] of NH_2 group which show the presence of NH_2 group in all these compounds. All the compounds absorb between 3025-3000 cm^{-1} due to stretching vibration of aromatic C-H bond[26-28]. Two bands appearing at 1620-1600 and 1505-1485 cm^{-1} are safely assigned to ν_{sym}(C=C) of benzene ring in IR spectra of all the compounds which shows the evidence of the presence of benzene ring in all the compounds. The sharp bands between 2951-2900 and 2890-2860 cm^{-1} are assigned to ν_{asym}(C-H) and ν_{sym}(C-H) of methyl group *i.e.* aliphatic C-H bond[29-32]. The infrared band at 1300-1290 cm^{-1} may be assigned to ν(N-C) (aromatic) in compound **1, 5, 6, 7, 8, 9** and **10**[33-36]. This absorption frequency is higher than the stretching frequency of N-C(meth.) (1250 cm^{-1}) because there is a little π-bond character in N-C (arom.) bond due to resonance.

TABLE-1
CHARACTERISTICS DATA OF THE SOME TELLURO COMPOUNDS

Compd. No.	Compounds (colour)	m.p. (°C)	Elemental analysis (%): Found (calcd.)					
			C	H	Cl	Te	Hg	N
1	2-(Chloromercury)aniline	163	21.98	1.83	10.83	–	61.06	4.27
	(White)		(22.15)	(2.00)	(10.54)		(60.92)	(3.71)
2	4-Methylphenyl $TeCl_3$	95	26.04	2.17	3.02	38.76	–	4.35
	(Pale yellow)		(26.39)	(2.05)	(2.90)	(38.53)		(4.30)
3	4-Ethylphenyl $TeCl_3$	96	28.52	2.67	32.65	37.15	–	–
	(Pale yellow)		(28.80)	(2.53)	(31.42)	(37.00)		
4	Phenyl $TeCl_3$	98	26.37	14.83	26.00	45.79	–	–
	(White)		(26.55)	(1.64)	(26.21)	(45.34)		
5	2-(Cl_2TeAr) aniline	175	39.45	3.01	19.45	34.04	–	3.83
	(Pale yellow crystalline solid)		(39.96)	(3.00)	(18.73)	(33.48)		(3.70)
6	2-(Cl_2Te-4-MeC_6H_4)-P-aniline	219	41.16	3.43	18.73	32.98	–	3.69
	(Pale yellow crystalline solid)		(41.38)	(3.25)	(18.62)	(32.79)		(3.47)
7	2-(Cl_2Te-4-Et C_6H_4)-aniline	193	42.74	3.81	18.06	31.80	–	3.56
	(Yellow crystalline solid)		(42.85)	(4.00)	(17.92)	(31.69)		(3.48)
8	2-(Te- C_6H_5) aniline	–	48.97	3.74	–	42.51	–	4.76
	(Yellow dense oil)		(50.00)	(3.68)		(42.43)		(4.59)
9	2-(Te-4-MeC_6H_4) aniline	75	50.64	4.22	–	40.58	–	4.54
	(Yellow crystalline)		(50.87)	(4.31)		(40.29)		(4.38)
10	2-(Te-4-Et-C_6H_4) aniline	98	52.17	4.66	–	38.81	–	4.35
	(Bright yellow)		(52.38)	(4.79)		(38.63)		(4.26)

TABLE-2
ASSIGNMENT OF KEY IR BANDS (cm^{-1}) IN TELLURO COMPOUNDS

Vibrational mode	Compounds									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
ν_{asym}(NH)	3410	–	–	–	3400	3410	3383	3398	3400	3410
ν_{sym}(NH)	3188	–	–	–	3200	3195	3190	3190	3200	3200
ν_{aro}(C-H)	3000	3010	3015	–	3005	3000	3005	3020	3010	3015
ν_{aliph}(C-H)	2910	2910	2900	3025	2900	2910	2900	2905	2915	2900
	2870	2875	2870	–	2890	2890	2872	2880	2860	2870
ν(C-C)	1600	1610	1600	1615	1600	1610	1605	1610	1620	1615
	1495	1495	1490	1485	1495	1490	1500	1505	1500	1485
ν_{aro}(N-C)	1300	–	–	–	1305	1290	1310	1300	1305	1310
ν(C-H) bending out-of-plane	727	725	730	725	730	720	700	715	715	724
	693	690	695	695	690	690	695	690	680	692
ν(Te-Cl)	–	290	285	285	280	285	290	–	–	–
ν(Te-C)	–	280	285	280	280	300	290	290	290	305
		–	–	–	250	265	260	255	260	265

In far infrared region a band appears at 290-280 cm^{-1} in compounds **2, 3, 4, 5, 6** and **7** which disappear in compounds **8**, **9** and **10**. Subsequently this band is assigned to ν(Te-Cl) vibration[37-41]. The bands appearing at 265-250 and 350- 280 cm^{-1} in the far IR region in all the compounds except no **1** are assigned to ν(Te-C) (aro) stretching vibration. In compounds **5, 6, 7, 8, 9** and **10** the band appears as closely spaced doublet. In these compounds. Te is attached to two aromatic rings occupying the two equatorial positions around Te. Since, the two Te-C (arom.) bond vibrations may interact producing two closely spaced bands. It, however, is not Fermi resonance but like that[42-46].

NMR spectra: Important ^{1}H NMR peaks of compounds are given in Table-3. In ^{1}H NMR spectra of the methyl protons flip at $\delta = 2.29$ (s) while NH$_2$ protons absorb at $\delta = 3.8$ ppm as singlet. Due to anisotropic effect of benzene ring methyl protons are deshielded and hence flip at downfield in respect of that of aliphatic CH$_3$ group[47-50]. In aniline two doublets *i.e.* $\delta = 6.60$-6.68 and 6.37-7.06 ppm appear due to H$_a$ and H$_b$, respectively. Both the signals are doublet due to spin-spin interaction with their adjacent protons which is well expected for an 'AA' 'BB' spin system. Since NH$_2$ group is *ortho* and *para* directing, the electrophilic substitution in aniline is possible only at *ortho* position to NH$_2$. Hence on mercuration only monomercurated derivative is obtained as it is evident from its solubility in chloroform[51]. This could further be substantiated by the appearance of unresolved multiplet around $\delta = 7.06$-7.25 ppm due to deshielded phenyl protons in ^{1}H NMR spectrum of the mercurated derivative of aniline (compound **1**). In compounds **5-10**, the NH$_2$ protons flip at 4.00-4.10 ppm which is *ca.* 0.2 ppm down field compared to mercurated aniline. It shows that NH$_2$ protons are a bit more deshielded in these telluro compounds. This deshielding may probably be partly contributed by the greater involvement of N of NH$_2$ group in the secondary interaction with Te(IV) compared to Hg(II) as the former is more electron attracting due to greater +ve charge on it and also due to its greater electronegativity than Hg. In telluro compounds, the phenyl protons show very complex pattern. The protons *ortho* to tellurium resonate at down field *i.e.* around $\delta = 8$ ppm relative to the other phenyl protons. This may be attributed to the fact that the *ortho* proton are more affected by Te(IV), a center of higher electronegativity and also the higher charge causing greater deshielding of its *ortho* proton by pulling the electron cloud towards itself. The compounds containing ethyl group such as compounds **3**, **7** and **10**, a quartet is observed at $\delta = 1.96$-4.17 ppm. while a triplet is observed at $\delta = 1.36$-1.50 ppm. The former is assigned to CH$_2$ protons which are more deshielded due to greater electron pulling nature of benzene ring and hence flip at down field in respect to methyl protons. As CH$_2$ protons sigma experiences four different magnetic field of three protons of the adjacent CH$_3$ group by spin-spin interaction and subsequently the signal splits up into quartet. Similarly, the protons of CH$_3$ group is affected by the spin arrangements of two protons of its adjacent CH$_2$ group and hence splits into triplet. Thus ^{1}H NMR spectra confirm the presence of ethyl group in compounds **3, 7** and **10**. In comounds **2**, **6** and **9** a singlet is observed due to flipping of methyl protons at 3.8-3.9 ppm which shows the presence of methyl group in these compounds.

TABLE-3
^{1}H NMR PEAKS (δ ppm) OF COMPONENTS

Compd. No.	Compounds	Me	NH_2	Me/Et	Aromatic protons
1	Aniline	–	3.81	–	7.06-7.25, H_a, H_b & H_C
2	4-Methyl phenyl $TeCl_3$	–	–	3.8	7.00-7.5
3	4-Ethyl phenyl $TeCl_3$	–	–	3.96-4.17 (q), (CH_2), 1.5(t) CH_3	7.05-7.29, H(Ar)
4	Phenyl $TeCl_3$	–	–	–	7.00-7.35, H(Ar)
5	2-(Cl_2TeAr) aniline	2.28(s)	4.10	–	7.15-8.45 (H_a-H_f)
6	2-(Cl_2Te-4-MeAr) aniline	2.26(s)	4.10	3.90	7.07-7.35-H(Ar) 8.25-8.34 H(Ar)
7	2-(Cl_2-Te-4'-ethyl Ar) aniline	2.28(s)	4.01	3.90-4.15(q), CH_2 1.48(t), CH_3	7.05-7.34 (Ha,Hc&He,) 8.25-8.34(d), (Ar)
8	2-(Te-C_6H_5)-Aniline	2.10(s)	3.9	–	6.95(s), Ha, 7.05(s) Hb, 6.48(s) Hc, 7.27-7.34-He & Hf, 7.87-Hd.
9	2-(Te-4'-MeC_6H_4) Aniline	2.11(s)	3.95	3.82	6.86(s)-Ha,7.05(s)-Hb, 6.49(s) Hc, 6.74(d), He, 7.71(d)-Hd.
10	2-(Te-4'-EtC_6H_4) Aniline	2.11(s)	3.95	3.93-4.14(CH_2) 1.38-1.50(t) CH_3	6.84(s)-Ha, 6.92(s)Hb 6.49(s)-Hc, 6.7(d)-He, 7.78(d)-Hd.

After the reduction of compounds **5**, **6** and **7** by removing two Cl^- ions on Te into tellurides there is a significant change in the position of NH_2 protons which become a little more shielded due to decrease in oxidation number of Te from +4 to +2. The aromatic protons *ortho* to Te in compound **8**, **9** and **10** experience more shielding due to the presence of two lone pairs of electrons on Te and hence appears at slightly up field *i.e.* at δ = 6.48-6.49 ppm as a singlet. The shielding of Hd protons, also *ortho* to Te is relatively less (0.5 ppm).

Thus on the basis of the foregoing discussion, it is quite reasonable to conclude that IR spectral bands and ^{1}H NMR data are in the favour of the formation of the telluro compounds.

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