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2,2,2-TRIFLUOROETHYL ARYL TELLURIDES, $ArTeCH_2CF_3$ AND THEIR DERIVATIVES $Ar(CF_3CH_2)TeX_2$(Ar = C_6H_5, p-$CH_3C_6H_4$; X = Cl, OCH_2CF_3): PREPARATION AND CHARACTERIZATION

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SUMMARY

2,2,2-Trifluoroethyl aryl tellurides, viz; $C_6H_5TeCH_2CF_3$ and p-$CH_3C_6H_4TeCH_2CF_3$ are prepared in high yields by reacting alkylating agent (2,2,2-trifluoroethyl tosylate or 2,2,2-trifluoroethyl iodide) with aryl tellurolate anion generated *in situ*. These tellurides have been converted to their corresponding tellurium dichlorides which on further treatment with $NaOCH_2CF_3$ in CF_3CH_2OH medium gave the corresponding bis(2,2,2-trifluoroethoxides). These compounds have been characterized by elemental analyses, IR, ^1H and ^{19}F NMR and mass spectra.

INTRODUCTION

Perfluoroalkyl derivatives of tellurium are a little studied class among organotellurium compounds [1-11]. One of the potential uses of such perfluoroalkyl substituted ligands is the fine tuning of the electronic properties of a metal complex [6]. A number of synthetic procedures is available for the preparation of trifluoromethyl derivatives of groups 15 and 16 [6]. In continuation of our work on organotellurium compounds [12,13], we now report a

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facile synthesis of the previously unknown tellurides, viz; $C_6H_5TeCH_2CF_3$ and $p\text{-}CH_3C_6H_4TeCH_2CF_3$ and their dichlorides and trifluoroethoxides. The scheme used for the preparation of these tellurides is similar to that used for the preparation of their selenium analogues [14,15]. To the best of our knowledge, such a scheme has not been previously used for the preparation of tellurides.

RESULTS AND DISCUSSION

Aryl tellurolate anions are valuable intermediates in synthetic chemistry [1-4, 16, 17]. Generally such anions are generated by the reduction of diaryl ditellurides with sodium tetrahydroborate. An attempt to react aryl tellurolate anion (generated by reduction of diaryl ditelluride with sodium tetrahydroborate) with 2,2,2-trifluoroethyl tosylate in ethanol to prepare the desired tellurides was not successful. We observed that sodium metal can reduce diaryl ditellurides in dry refluxing tetrahydrofuran to aryl tellurolate anions which further react with 2,2,2-trifluoroethyl tosylate in the presence of hexamethylphosphoric triamide to produce the desired tellurides. However, the compounds were obtained in low yields ($\sim$ 20%), whereas in case of analogous selenium compounds the yields reported are high [14].

$$1/2\ Ar_2Te_2 \xrightarrow[THF]{Na} ArTeNa \xrightarrow[HMPA]{CF_3CH_2OTos} \underset{(A,\ B)}{ArTeCH_2CF_3} + NaOTos$$

Better yields were realised when 2,2,2-trifluoroethyl iodide was used as alkylating agent in place of tosylate under the same reaction conditions.

$$1/2\ Ar_2Te_2 \xrightarrow[THF]{Na} ArTeNa \xrightarrow[HMPA]{CF_3CH_2I} \underset{(A,\ B)}{ArTeCH_2CF_3} + NaI$$

Ar = C_6H_5, $p\text{-}CH_3C_6H_4$.

This method affords a convenient synthesis to obtain partially fluorinated alkyl aryl tellurides in better yields and can be extended to the preparation of numerous alkyl aryl tellurides.

2,2,2 -Trifluoroethyl aryl tellurides are yellowish liquids, soluble in common organic solvents but immiscible with water. These compounds are stable for weeks as compared to the non-fluorinated alkyl aryl tellurides which start decomposing after few days [18].

2,2,2 -Trifluoroethyl aryl tellurides react with sulfuryl chloride in chloroform to give 2,2,2-trifluoroethyl aryl tellurium(IV) dichlorides (C, D). These dichlorides are white crystalline solids soluble in polar solvents. The metathesis between 2,2,2-trifluoroethyl aryl tellurium(IV) dichlorides and sodium trifluoroethoxide in trifluoroethanol yields the respective trifluoroethoxides (E,F).

$$ArTeCH_2CF_3 \xrightarrow[CHCl_3]{SO_2Cl_2} \underset{(C,\ D)}{\begin{matrix} Cl \\ | \\ ArTeCH_2CF_3 \\ | \\ Cl \end{matrix}} \xrightarrow[CF_3CH_2OH]{2CF_3CH_2ONa} \underset{(E,\ F)}{\begin{matrix} OCH_2CF_3 \\ | \\ Ar\text{-}TeCH_2CF_3 \\ | \\ OCH_2CF_3 \end{matrix}}$$

These trifluoroethoxides are feebly hygroscopic, faintly colored, viscous liquids and soluble in common organic solvents. The compositions of compounds A-F were established primarily by elemental analyses (Table 1). Their IR, ^1H and ^{19}F NMR and mass spectral data are given in the experimental section.

TABLE 1

Compound	m.p. or b.p. (°C)/torr	Yield (%)	Analysis Found (Calcd) % C	H	Cl	Te
(A) $C_6H_5TeCH_2CF_3$	80/5	80 (20)[a]	33.2 (33.4)	2.2 (2.4)	--	44.9 (44.3)
(B) $p\text{-}CH_3C_6H_4TeCH_2CF_3$	120/2.5	80 (20)[a]	35.7 (35.8)	2.7 (3.0)	--	42.5 (42.3)
(C) $C_6H_5(CF_3CH_2)TeCl_2$	85	77	26.5 (26.7)	1.7 (1.9)	19.7 (19.8)	35.7 (35.6)
(D) $p\text{-}CH_3C_6H_4(CF_3CH_2)TeCl_2$	95	80	28.6 (28.9)	2.3 (2.4)	18.9 (19.0)	34.5 (34.2)
(E) $C_6H_5(CF_3CH_2)Te(OCH_2CF_3)_2$	18	77	29.4 (29.5)	2.1 (2.2)	--	26.5 (26.3)
(F) $p\text{-}CH_3C_6H_4(CF_3CH_2)Te(OCH_2CF_3)_2$	20	76	31.1 (31.2)	2.5 (2.6)	--	25.7 (25.5)

[a] when 2,2,2-trifluoroethyl tosylate was used as an alkylating agent.

The presence of several stable isotopes of naturally occurring tellurium [19] leads to highly characteristic patterns consisting of a group of peaks for tellurium containing fragments in their mass spectra. The major fragments observed for the present compounds are given in the experimental section based on ^{1}H, ^{12}C, ^{16}O, ^{19}F, ^{35}Cl and ^{130}Te isotopes. Molecular ion peaks are observed in case of 2,2.2-trifluoroethyl aryl tellurides. Peaks corresponding to M^{+} in 2,2,2-trifluoroethyl aryl tellurium (IV) dichlorides and bis(trifluoroethoxides) were not observed. However, peaks corresponding to $CF_3CH_2(Ar)TeX^{+}$ ions (X = Cl or OCH_2CF_3), are observed as highest m/z species.

EXPERIMENTAL

Materials and methods

Diaryl ditelluride [20] 2,2,2-trifluoroethyl iodide [21] and 2,2,2-trifluoroethyl tosylate [21] were prepared by literature methods. Sodium trifluoroethoxide was prepared by reacting sodium with excess trifluoroethanol. Tetrahydrofuran (THF) was dried over sodium metal. All other chemicals were of reagent grade and used as such.

The IR spectra were recorded either as neat liquids or Nujol mulls between KBr/AgCl/CsI plates on a Perkin Elmer-1430 spectrophotometer. ^{1}H and ^{19}F NMR spectra were recorded on a Varian model EM-390 spectrometer using tetramethylsilane (TMS) as internal and $CFCl_3$ as external reference, respectively. EI mass spectra were obtained on a VG Micromass 7070 F at 70 eV. All melting and boiling points are uncorrected. Tellurium and chlorine were determined by standard methods [22]. Carbon and hydrogen were determined microanalytically.

Preparation of 2,2,2-trifluoroethyl aryl tellurides

A mixture of sodium (0.46 g, 0.20 mmol) and diaryl ditelluride (10 mmol) was refluxed in 50 ml of dry tetrahydrofuran for 4.5 h. The contents were allowed to cool to room temperature. Hexamethylphosphoric triamide (2 ml) followed by alkylating agent (20 mmol of 2,2,2-trifluoroethyl tosylate or 25 mmol of trifluoroethyl iodide) in 10 ml of tetrahydrofuran were slowly added to the reaction mixture and refluxed for 5 h in a dry deoxygenated nitrogen atmosphere. The cooled reaction mixture was poured into water (50 ml) and extracted with diethylether (4 x 25 ml). The combined ethereal extracts were washed with 5% aqueous sodium hydroxide (50 ml) and dried with magnesium sulfate. The solvents were removed under vacuum and telluride obtained by distillation in vacuo. Analytical data, yields and b.p. of the tellurides are given in Table 1.

$C_6H_5TeCH_2CF_3$(A): IR(liquid film) : 3065m, 3010w, 2960mw, 2875w, 1575ms, 1475ms, 1438m, 1410s, 1365w, 1344sh, 1325sh, 1305sh, 1275s, 1255ms, 1198s, 1160sh, 1095vs, 1060w, 1038ms, 1000w, 938w, 910w, 840ms, 810w, 775vw, 738vs, 695s, 630ms, 508w, 455ms, 355m, 282ms, 258m cm^{-1}.

^1H and ^{19}F NMR (CCl_4) : δ_H 3.3(q, $\underline{CH_2}CF_3$), 7.30-7.90(m, $C_6\underline{H_5}$); δ_F -61.0(t, $CH_2\underline{CF_3}$)ppm.

MS(EI) : m/z 290(100)M^+, 213(2)$CF_3CH_2Te^+$, 207(85)$C_6H_5Te^+$, 160(1)$C_6H_5CH_2CF_3^+$, 130(2.2) Te^+, 77(98)$C_6H^+_5$.

p-$CH_3C_6H_4TeCH_2CF_3$ (B): IR(liquid film) : 3070sh, 3025mw, 2960w, 2930m, 2875w, 1488m, 1462mw, 1410m, 1390w, 1365sh, 1342sh, 1305w, 1275s, 1255s, 1195s, 1095sb, 1040s, 1015w, 942w, 838m, 802s, 778mw, 658w, 630s, 575vw, 530w, 482s, 355m, 280ms, 240ms cm^{-1}.

^1H and ^{19}F NMR (CCl_4): δ_H 3.3(q, $C\underline{H}_2CF_3$), 2.33(s, $C\underline{H}_3$), 7.10 - 7.83(d, $c_6\underline{H}_4$); δ_F -61.0(t, $CH_2C\underline{F}_3$)ppm.

MS(EI): m/z 304(48.7)M^+, 221(58.9)$CH_3C_6H_4Te^+$, 213(2)$CF_3CH_2Te^+$, 174(1)$CH_3C_6H_4CH_2CF^+_3$, 130(1)Te^+, 91(100)$CH_3C_6H_4^+$.

Preparation of 2,2,2-trifluoroethyl aryl tellurium(IV) dichlorides

Sulfuryl chloride (2.43 g, 18 mmol) was added dropwise to the stirred solution of 2,2,2-trifluoroethyl aryl telluride (12 mmol) in 25 ml of chloroform over a period of 15 min. The contents were stirred at room temperature for 1 h. Removal of solvents under vacuum leaves behind a residual white mass. Recrystallisation of the white residual mass from chloroform affords pure white crystalline 2,2,2-trifluoroethyl aryl tellurium(IV) dichloride. Analytical data, m.p. and yields of these chlorides are given in Table 1.

$C_6H_5(CF_3CH_2)TeCl_2$(C): IR(Nujol mull): 1576w, 1332w, 1276m, 1260m, 1202ms, 1116m, 1050m, 996mw, 914w, 842w, 770w, 730m, 680m, 630mw, 530w, 510w cm^{-1}.

^1H and ^{19}F NMR ($CDCl_3$): δ_H 4.3(q, $C\underline{H}_2CF_3$), 7.83 - 8.46(m, $C_6\underline{H}_5$); δ_F -56.0(t, $CH_2C\underline{F}_3$)ppm.

MS(EI): m/z 325(20)$C_6H_5(CF_3CH_2)TeCl^+$, 290(33.6)$C_6H_5TeCH_2CF^+_3$, 248(13.6)$CF_3CH_2TeCl^+$, 242(20.3)$C_6H_5TeCl^+$, 130(2)Te^+, 112(30)$C_6H_5Cl^+$, 77(100)$C_6H_5^+$.

$p\text{-}CH_3C_6H_4(CF_3CH_2)TeCl_2$ (D):IR(Nujol mull): 1588w, 1558w, 1314m, 1258m, 1200m, 1116m, 1044mw, 1030mw, 1006mw, 838mw, 722m, 628m, 480ms cm^{-1}.

^1H and ^{19}F NMR ($CDCl_3$): δ_H 2.5(s,$\underline{CH}_3$), 4.3(q, $\underline{CH}_2CF_3$), 7.56-8.3(d,C_6H_4); δ_F -56.0(t, $CH_2\underline{CF}_3$)ppm.

MS(EI): m/z 339(15)$CH_3C_6H_4(CF_3CH_2)TeCl^+$, 304(30)$CH_3C_6H_4TeCH_2CF_3^+$, 256(20)$CH_3C_6H_4TeCl^+$, 248(11)$CF_3CH_2TeCl^+$, 221(60)$CH_3C_6H_4Te^+$,130(2.1)$Te^+$, 126(25)$CH_3C_6H_4Cl^+$, 91(100)$CH_3C_6H_4^+$.

Preparation of 2,2,2-trifluoroethyl aryl tellurium(IV) bis(trifluoroethoxides)

A solution of sodium trifluoroethoxide (2.44 g, 20 mmol) in trifluoroethanol (10 ml) was added to the stirred solution of 2,2,2-trifluoroethyl aryl tellurium(IV) dichloride (10 mmol) in 10 ml of trifluoroethanol. The reaction mixture was stirred for 5 h at ambient temperature. The precipitated sodium chloride was filtered off and the solvent removed from the filtrate under vacuum. The resulting viscous mass was treated with 20 ml of petroleum ether ($40-60^o$) and filtered to remove insoluble materials if any. Removal of the solvent in vacuum yielded the required trifluoroethoxides as faintly coloured (creamish) semi solids. Analytical data, m.p. and yields of the prepared trifluoroethoxides are given in Table 1.

$C_6H_5(CF_3CH_2)Te(OCH_2CF_3)_2$ (E): IR(liquid film) 3062m, 3024w, 2958mw, 1574w, 1478m, 1440m, 1406ms, 1276sb, 1202mw, 1150m, 1108m, 1048m, 998mw, 944w, 844w, 738ms, 686sh, 634ms cm^{-1}.

^{1}H and ^{19}F NMR (CCl_4): δ_H 3.9(m, $C\underline{H}_2$ and $OC\underline{H}_2$), 7.7-8.15(m,$C_6\underline{H}_5$) δ_F - 56.6(t, $TeCH_2C\underline{F}_3$), -78.0(t, $OCH_2C\underline{F}_3$) ppm.

MS(EI): m/z 389(21)$C_6H_5(CF_3CH_2)TeOCH_2CF_3^+$, 312(8)$CF_3CH_2TeOCH_2CF_3^+$, 306(10)$C_6H_5TeOCH_2CF_3^+$, 290(30.2)$C_6H_5TeCH_2CF_3^+$, 213(2)$CF_3CH_2Te^+$, 207(60.2)$C_6H_5Te^+$, 176(3.1)$C_6H_5OCH_2CF_3^+$, 154(10.2)$C_{12}H_{10}^+$, 77(100)$C_6H_5^+$.

p-$CH_3C_6H_4(CF_3CH_2)Te(OCH_2CF_3)_2$ (F): IR(liquid film): 3058m, 3022w, 2968m, 2924ms, 2868mw, 1590mw, 1490ms, 1448m, 1394mw, 1378m, 1276s, 1208m, 1188m, 1152sb, 1118ms, 1092s, 1062ms, 1040w, 1012mw, 958m, 914w, 826m, 802s, 756ms, 730m, 642sb, 578w cm^{-1}.

^{1}H and ^{19}F NMR (CCl_4): δ_H 2.4(s, $C\underline{H}_3$), 3.9(m, $C\underline{H}_2$ and $OC\underline{H}_2$), 7.43-7.86(d, $C_6\underline{H}_4$); δ_F - 56.6(t, $TeCH_2C\underline{F}_3$), -78.0(t, $OCH_2C\underline{F}_3$) ppm.

MS(EI): m/z 403(28.1) $CH_3C_6H_4(CF_3CH_2)TeOCH_2CF_3^+$, 320(12)$CH_3C_6H_4TeOCH_2CF_3^+$, 312(6.2)$CF_3CH_2TeOCH_2CF_3^+$, 213(2) $CF_3CH_2Te^+$, 190(2.1)$CH_3C_6H_4OCH_2CF_3^+$, 182(12.2)$C_{14}H_{14}^+$, 91(100)$CH_3C_6H_4^+$.

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