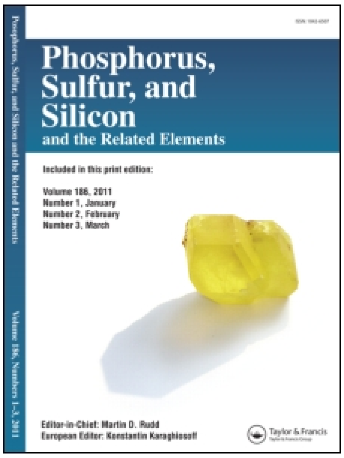

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NEW ALIPHATIC TELLURENYL AND TELLURINYL COMPOUNDS

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Abstract Continuing earlier work on organyl tellurium halides[1], alkyl tellurium trihalides $RTeHal_3$ (Hal = Cl, Br, I) and salts incorporating the alkanetetrahalotellurinate anions $A^+RTeHal_4^-$ (A^+ = py^+, $NR'_4{}^+$; Hal = Cl, Br, I) have been synthesized. The equimolar reaction of R_2Te_2 with elemental halogen yielded the aliphatic tellurenyl halides RTeHal (Hal = Cl, Br, I), that were also accessible by the comproportionation of R_2Te_2 and $RTeHal_3$. The tellurenyl compounds were trapped chemically and characterized spectroscopically. Hydrolysis of the trihalides afforded various tellurinyl derivatives, depending on the reaction conditions: RTe(O)Hal (Hal = Cl, Br), $RTeO_2^-$, or $(RTeO)_2O$. Constitutions and equilibria were studied by NMR, UV, CD, MCD, and IR.

Aliphatic Tellurium Dihalides $RR'TeHal_2$, Trihalides $RTeHal_3$, and Tetrahalotellurinates $RTeHal_4^-$

In order to investigate the reactions and the spectroscopic properties of the incompletely studied aliphatic tellurium di- and trihalides, we had at first to synthesize and to characterize suitable compounds. The reaction of *n*-dialkyl ditellurides (some of them new) with an excess of the free halogens Cl_2, Br_2, or I_2, respectively, provided the necessary *n*-alkyl tellurium trihalides. The incorporation of longer chains like octyl, decyl, or dodecyl improved the solubility of the products and facilitated thereby their full characterization, at the same time eliminating odor problems. Bromination with pyridinium tribromide continued to the pyridinium alkanetetrahalotellurinate stage, thus providing a new class of compounds. Another straightforward route to these anions was found in the reaction of $RTeHal_3$ with ionic halides.

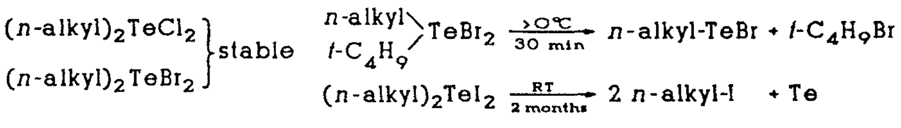
$$
\begin{aligned}
R_2Te_2 &+ 3\,Hal_2 \longrightarrow 2\,RTeHal_3 \\
R_2Te_2 &+ 3\,py^+Br_3^- \longrightarrow 2\,py^+RTeBr_4^- + py^+Br^- \\
RTeHal_3 &+ A^+Hal^- \longrightarrow A^+RTeHal_4^-
\end{aligned}
$$

(Hal = Cl, Br, I, A^+ = py^+, tetraalkylammonium, R = *n*-alkyl)

The chloro and the bromo compounds are usually stable, but with $RTeI_3$ and $RTeI_4^-$ the decomposition of a solution thereof is apparent already after storage at room temperature for a few hours, leading to alkyl iodides and inorganic matter and also to minor quantities of R_2TeI_2.

Dialkyl tellurium dihalides were synthesized by the reaction of aliphatic monotellurides with the elemental halogens; the compounds $RR'TeHal_2$ are liquids or low melting solids, the stability of which depends markedly on the alkyl group and on the halogen:

$$RR'Te + Hal_2 \longrightarrow RR'TeHal_2 \qquad (Hal = Cl, Br, I;\ R,R' = \text{alkyl})$$



$$\left.\begin{array}{l}(n\text{-alkyl})_2TeCl_2\\(n\text{-alkyl})_2TeBr_2\end{array}\right\}\text{stable} \qquad \begin{array}{l}\begin{matrix}n\text{-alkyl}\\t\text{-}C_4H_9\end{matrix}\!\!>TeBr_2 \xrightarrow[30\ \text{min}]{>0°C} n\text{-alkyl-TeBr} + t\text{-}C_4H_9Br\\(n\text{-alkyl})_2TeI_2 \xrightarrow[2\ \text{months}]{RT} 2\ n\text{-alkyl-I} + Te\end{array}$$

Aliphatic Tellurenyl Halides RTeHal

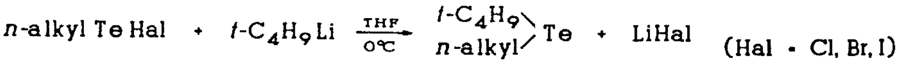
The reaction of R_2Te_2 with Hal_2 in the molar ratio 1 : 1 led to the formation of the not previously reported aliphatic tellurenyl halides RTeHal. Although no crystalline samples could be obtained so far, and despite thermal decomposition to R_2TeHal_2 and tellurium, the stabilities are high enough in all cases to enable carrying out spectroscopic investigations and chemical reactions; whereas the iodides RTeI decompose within minutes at room temperature, the chlorides RTeCl are stable for weeks. Even more convenient is the preparation of the alkanetellurenyl halides by the comproportionation reaction of dialkyl ditellurides with alkyl tellurium trihalides leading to an equilibrium that lies far on the side of the tellurenyl moiety: Just mixing of the solutions of the components is all that is needed.

$$R_2Te_2 + Hal_2 \longrightarrow 2\,RTeHal \longrightarrow Te + R_2TeHal_2$$

$$R_2Te_2 + RTeHal_3 \rightleftharpoons 3\,RTeHal$$

$$\text{stabilities: } RTeCl > RTeBr > RTeI \qquad (Hal = Cl, Br, I;\ R = n\text{-alkyl})$$

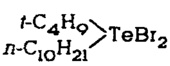
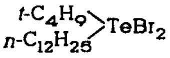
The tellurenyl halides can be trapped in excellent yield by alkyl lithiums, thus providing a new access to unsymmetrical aliphatic tellurides, *e.g.*,:



$$n\text{-alkyl TeHal} + t\text{-}C_4H_9Li \xrightarrow[0°C]{THF} \begin{matrix}t\text{-}C_4H_9\\n\text{-alkyl}\end{matrix}\!\!>Te + LiHal \qquad (Hal = Cl, Br, I)$$

Detailed investigations of the comproportionation reaction by UV/VIS techniques have not indicated the formation of any complexes or compounds of different stoichiometry but RTeHal, despite a large excess of either $RTeHal_3$ or R_2Te_2 in the reaction mixture, wheras NMR-spectra show a rapid exchange that broadens or renders undetectable the α-, the β-, and even the γ-carbon atoms of the 3 components in equilibrium at room temperature. Employing low temperatures and high magnetic fields (*e.g.*, −90 °C in CD_2Cl_2 on a 500 MHz NMR instrument), the ^{13}C NMR spectra of the pure tellurenyl halides indicate that still another exchange process is involved, since eventually two sets of carbon resonances in a 1 : 1 ratio are obtained, differing by some 20 ppm for δ (C-α). Similarly, the tellurium resonance splits into two signals at low temperatures. The origin of this event is still uncertain.

TABLE I Physical data for representative aliphatic tellurium halides.

compound	mp. /℃	color	$\delta^{125}Te$ ppm	$\Delta_{1/2}$ Hz	$\delta^{13}C^{\bullet}$ ppm	$^1J(\underline{Te}\text{-}\underline{C}H_2)$ Hz	$\delta^{13}C^{+}$ ppm	$\delta^1H^{\#}$ ppm
$(n\text{-}C_8H_{17})_2TeCl_2$	~ -10	colorless	875^a	10	46.5^a	163	25.1	3.48^a
$(n\text{-}C_{10}H_{21})_2TeCl_2$	~ -10	colorless	873^a	10	46.6^a	165	25.2	3.44^a
$(n\text{-}C_{12}H_{25})_2TeCl_2$	~ -5	colorless	883^a	10	46.6^a		25.2	3.44^a
 $(t\text{-}C_4H_9)(n\text{-}C_{10}H_{21})TeBr_2$	×	yellow	1105^f	10	46.3^f	148(?)	26.0	
 $(t\text{-}C_4H_9)(n\text{-}C_{12}H_{25})TeBr_2$	×	yellow	1108^f	10	46.6^f		26.0	
$(n\text{-}C_8H_{17})_2TeBr_2$	~ -15	colorless	818^a	10	44.8^a	156	25.5	3.56^a
$(n\text{-}C_{10}H_{21})_2TeBr_2$	~ -10	colorless	817^a	10	44.8^a	153	25.5	3.59^a
$(n\text{-}C_{12}H_{25})_2TeBr_2$	~ -10	brownish	812^a	10	45.3^a	154	25.7	3.58^a
$(n\text{-}C_8H_{17})_2TeI_2$	~ -20	red	724^b	10	42.0^a	126	26.3	3.56^a
$(n\text{-}C_{10}H_{21})_2TeI_2$	~ -20	red	728^a	10	42.0^a	126	26.3	3.59^a
$(n\text{-}C_{12}H_{25})_2TeI_2$	30	red	720^b	10	41.6^b	124	26.5	3.55^a
$n\text{-}C_8H_{17}TeCl_3$	57	white	1552^a	20	60.5^a	213	25.2	3.99^a
$n\text{-}C_{10}H_{21}TeCl_3$	43	white	1557^a	20	60.8^a	205	25.2	3.95^a
$n\text{-}C_{12}H_{25}TeCl_3$	48-49	white	1558^a	20	60.9^a	206	25.2	3.99^a
$n\text{-}C_8H_{17}TeBr_3$	57	yellow	1463^a	30	56.9^a		27.2	4.08^a
$n\text{-}C_{10}H_{21}TeBr_3$	57	yellow	1468^a	30	56.7^a	185	27.3	4.08^a
$n\text{-}C_{12}H_{25}TeBr_3$	58	yellow	1467^a	30	56.8^a	183	27.3	4.09^a
$n\text{-}C_8H_{17}TeI_3$	91	violet, red in sol.	1284^b	150	46.6^b	148(?)	30.9	3.90^a
$n\text{-}C_{10}H_{21}TeI_3$	88	violet, red in sol.	1284^b	150				
$n\text{-}C_{12}H_{25}TeI_3$	83	violet, red in sol.	1285^b	150	46.5^b		30.9	3.89^a
$py^+ n\text{-}C_8H_{17}TeCl_4^-$	148	white	1321^c	60	66.7^c	183	26.4	3.68^c
$py^+ n\text{-}C_8H_{17}TeBr_4^-$	>300	yellow	1229^d	50	61.8^e	165	27.9	3.88^d
$py^+ n\text{-}C_{10}H_{21}TeI_4^-$	>300	green, red in sol.	963^c	80	51.2^c	118	30.5	3.73^d

(a) $CDCl_3$, (b) C_6D_6, (c) CD_3CN, (d) $(CD_3)_2CO$, (e) CD_3OD, (f) CD_2Cl_2, -20 ℃

• α-$\underline{C}H_2$, + β-$\underline{C}H_2$, # α-C$\underline{H}_2$, × viscous oil, stable only below 0 ℃

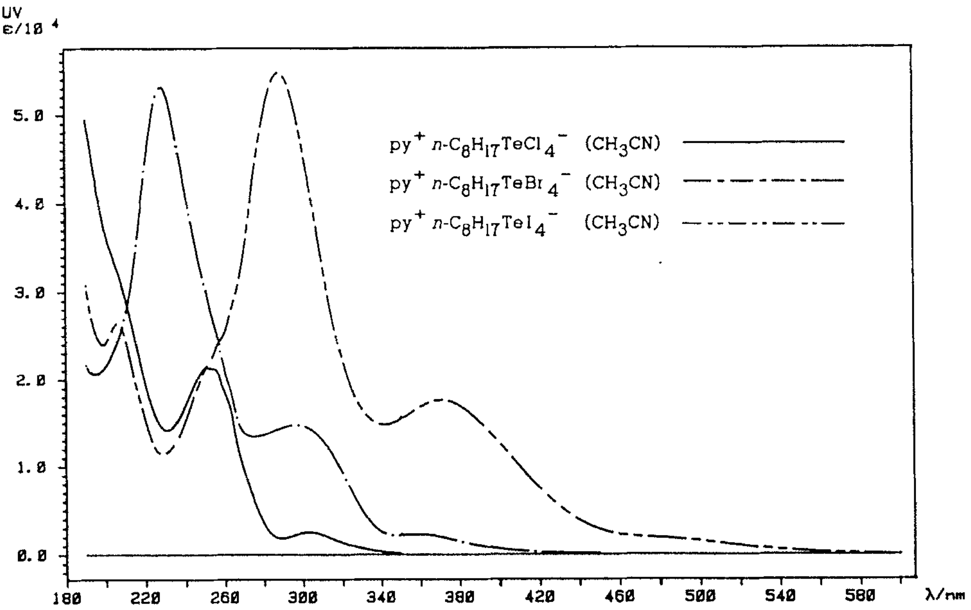


FIGURE 1 UV-spectra of pyridinium *n*-octanetetrahalotellurinates.

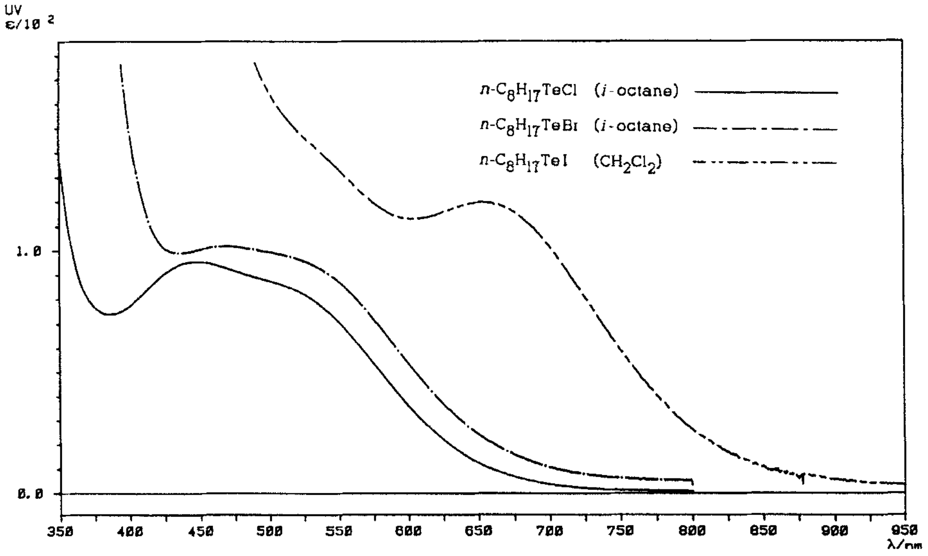


FIGURE 2 UV-spectra of n-octanetellurenyl halides.

TABLE II UV characteristics of some *n*-decyl tellurium compounds.

compound	solvent	λ_{max} (ε)	color
$(n\text{-}C_{10}H_{21})_2Te_2$	*i*-octane	258 sh (3150), 299 sh (393), 394 (615)	orange
$n\text{-}C_{10}H_{21}TeCl_3$	*i*-octane	207 (23600), 244 sh (8830), 298 (1650)	white
$n\text{-}C_{10}H_{21}TeCl$	*i*-octane	204 (16800), 231 sh (6490), 297 sh (1030) 450 (96), 516 sh (87)	cherry red
$n\text{-}C_{10}H_{21}TeBr_3$	*i*-octane	232 (38300), 280 sh (10600), 358 sh (1690)	yellow
$n\text{-}C_{10}H_{21}TeBr$	*i*-octane	300 sh (3000), 470 (102), 520 sh (98)	violet
$n\text{-}C_{10}H_{21}TeI_3$	CH_2Cl_2	281 (22300), 338 (12100), 460 sh (2210)	red
$n\text{-}C_{10}H_{21}TeI$	CH_2Cl_2	263 (4340), 286 (4080), 322 sh (2980) 531 sh (144), 653 (120)	green

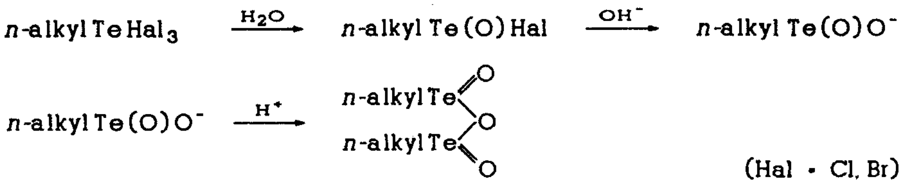
TABLE III NMR characteristics of *n*-octanetellurenyl chloride/bromide.

compound	T/°C	solvent	δ ^{13}C-NMR /ppm (TMS)			δ ^{1}H-NMR /ppm (TMS)	
			α-CH_2	β-CH_2	γ-CH_2	α-CH_2	β-CH_2
$n\text{-}C_8H_{17}TeCl$	-90	CD_2Cl_2	44.4 19.2	29.3 33.7	30.8 32.0	3.7 3.8	2.0
$n\text{-}C_8H_{17}TeCl$	0	$CDCl_3$	-	31.5*	31.5**		
$n\text{-}C_8H_{17}TeCl$	25	CD_2Cl_2				3.81	2.12
$n\text{-}C_8H_{17}TeBr$	-90	CD_2Cl_2	43.3 21.8	29.7 33.5	31.2 32.4	3.7 3.8	2.0
$n\text{-}C_8H_{17}TeBr$	25	C_6D_6	-	32^{+}	31.7^{++}		
$n\text{-}C_8H_{17}TeBr$	25	$CDCl_3$				3.79	2.06

$^{*}\Delta$ 1/2 - 70 Hz $^{**}\Delta$ 1/2 - 25 Hz $^{+}\Delta$ 1/2 - 20 Hz $^{++}\Delta$ 1/2 - 5 Hz

Aliphatic Tellurenyl Halides RTe(O)Hal, Tellurinates $RTeO_2^-$, and Tellurinic Acid Anhydrides $(RTeO)_2O$

By careful hydrolysis of alkyl tellurium trichlorides and tribromides, white powders with the composition of alkanetellurinyl halides RTe(O)Hal are obtained. The IR spectra are characterized by distinct absorption features in the 500 - 800 cm^{-1} region that change on prolonged boiling in alcohols. Further hydrolysis in aqueous alkaline media produces alkanetellurinate anions that deposit on acidification the poorly soluble anhydrides of the corresponding tellurinic acids. The structural investigation of these compounds is still in progress.



(Hal = Cl, Br)

Characterization of the Compounds

All compounds were prepared in good yields and gave correct elemental analyses (exception: RTeHal have not been analyzed). NMR, UV, and IR were used to elucidate the complex reactions and equilibria. In particular, ^{125}Te NMR is most useful for the characterization of the compounds, as chemical shifts, line widths and coupling constants vary in a typical manner with the substrates and their functionalities.

Most of the compounds show characteristic colors. Selected physical properties and spectral data of representative new organyl tellurium halides RR'TeHal$_2$, RTeHal$_3$, and RTeHal are collected in the Tables.

REFERENCES

1. D. Bendix, P. Laur, and I. K. Nielsen, Abstr. 4th Int. Conf. Org. Chem. Se and Te, Birmingham (GB) (1983); D. Bendix, Doctoral Dissertation, RWTH Aachen (1981)