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Synthesis and Characterization of Tellurocarboxylic Acid Salts and Bis(acyl) Ditellurides

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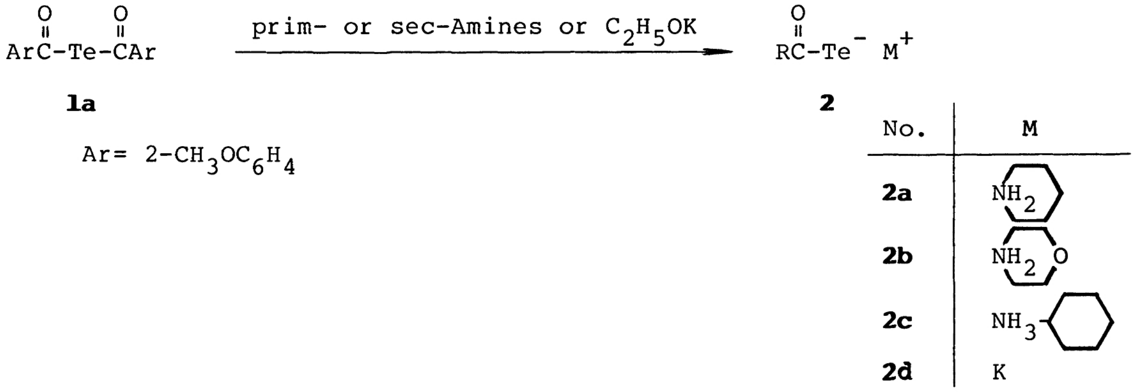
The reaction of bis(acyl) tellurides with primary or secondary amines or potassium ethanolate yielded the corresponding tellurocarboxylic acid salts, which are readily oxidized with iodine or benzenesulfonyl chloride to afford novel bis(acyl) ditellurides.

Similarly to carboxylic acid salts, tellurocarboxylic acid salts ($RCOTe^- M^+$) are considered to be one of the most fundamental and important starting compounds for the synthesis of tellurocarboxylic acid derivatives. However, due to their extreme instability, these compounds have never been described in literature so far.$^{1)}$ Recently we succeeded in isolation of bis(acyl) tellurides (**1**) (RCOTeCOR).$^{2)}$ The continuation of our effort led to the successful preparation of stable bis(acyl) telluride, bis(2-methoxybenzoyl) telluride (**1a**). Herein we report the synthesis and characterization of tellurocarboxylic acid salts (**2**), from the reaction of the telluride (**1a**) with primary or secondary amines or potassium ethanolate, as



$$\mathrm{Ar}\overset{O}{\overset{\|}{C}}\text{-Te-}\overset{O}{\overset{\|}{C}}\mathrm{Ar} \xrightarrow{\text{prim- or sec-Amines or } C_2H_5OK} \mathrm{R}\overset{O}{\overset{\|}{C}}\text{-Te}^-\ M^+$$

1a

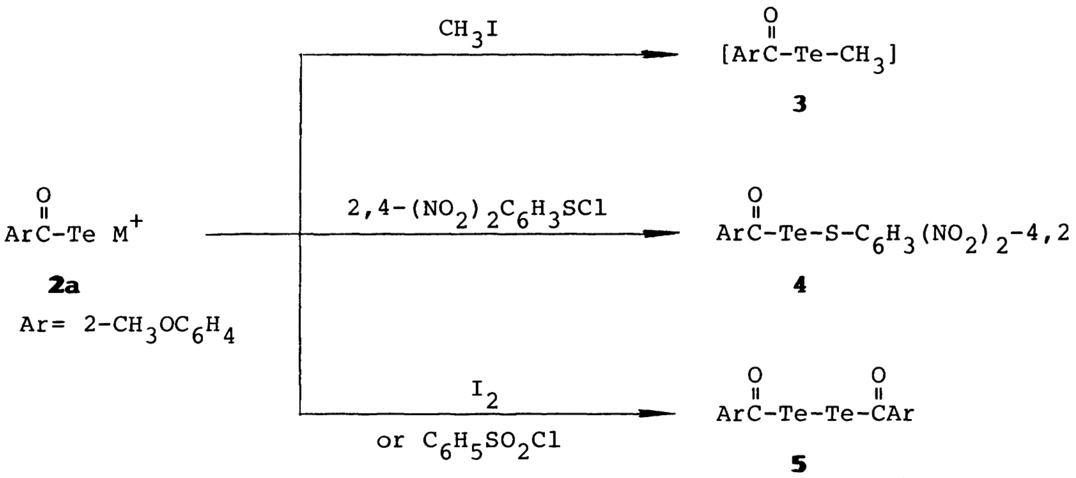
Ar= 2-$CH_3OC_6H_4$

2

well as the first isolation of novel bis(acyl) ditelluride (**5**).

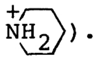
When two equivalents of piperidine in dichloromethane were added dropwise to a solution of bis(2-methoxybenzoyl) telluride (**1a**)$^{3)}$ at -30 °C under argon atmosphere, a slight yellow solution quikly changed to deep red, indicating the formation of piperidinium 2-methoxytellurobenzoate (**2a**)$^{4)}$ which showed a characteristic absorption maximum at 554 nm in visible region and a broad signal at δ8.7 which is attributable to $\overset{+}{N}H_2$ protons of piperidinium. Similarly, treatment of **1a** with morpholine, and cyclohexylamine, and potassium ethanolate gave deep red solution showing the formation of the corresponding ammonium (**2b**$^{5)}$ and **2c**$^{6)}$) and potassium salt (**2d**).$^{7)}$ These are the first observation of the tellurium isologues of carboxylic acid salt.

The tellurocarboxylic acid salts obtained were oily substances and too unstable thermally and toward oxygen to purify. Therefore, their constitutions were established by conversion into the methyl (**3**) and 2,4-dinitrobenzenesulfenyl esters (**4**). For example, the in situ formed piperidinium 2-methoxytellurobenzoate (**2a**) readily reacted with excess of methyl iodide at -30 °C to give methyl 2-methoxytellurobenzoate (**3**)$^{8)}$ as a yellow liquid. Under similar conditions, the reaction with 2,4-dinitrobenzenesulfenyl chloride afforded 32% of the corresponding sulfenyl ester (**4**)$^{9)}$ as yellow crystals.



No.	Ar
5a	2-$CH_3OC_6H_4$
5b	2-$CH_3C_6H_4$

The possibility of preparing novel bis(acyl) ditellurides (**5**) was explored. For example, the freshly prepared piperidinium salt (**2a**) was readily oxidized by iodine to give bis(2-methoxybenzoyl) ditelluride (**5a**) in 33% yield as red crystals.[10] In addition, a similar oxidation with benzenesulfonyl chloride instead of iodine led to over 50% yield of **5a**.[11] The reaction of piperidinium 2-methyltellurobenzoate with benzenesulfonyl chloride afforded the corresponding ditelluride (**5b**).[12] To our best knowledge, this is the first example of tellurium isologues of bis(acyl) peroxide.

The obtained bis(acyl) ditelluride (**5a**) is relatively stable thermally and toward moisture. No decomposition is observed even by refluxing in benzene under nitrogen atmosphere for a week. Interestingly, when piperidine was added to a solution of **5a** in dichloromethane at -70 °C, a yellow solution spontaneously changed to dark red and then to colorless with precipitation of black tellurium within 5 second, suggesting the formation of piperidinium 2-methoxypertelluro-benzoate (2-$CH_3OC_6H_4COTeTe^-$ 

).[13]

It is noted that the carbonyl resonance of the ditelluride (**5a**) shows upfield shift compared with those of the corresponding bis(acyl) disulfide and diselenide, while substitution of oxygen atom in acid anhydride by sulfur, selenium, and tellurium results in marked downfield shifts for carbonyl resonance (Table 1).

Table 1. Carbonyl resonances of chalcogeno isologues of bis(acyl) peroxide and acid anhydride

$R\overset{O}{\overset{\|}{C}}-E-E-\overset{O}{\overset{\|}{C}}R$		$^{13}C{=}O^{a)}$	$R\overset{O}{\overset{\|}{C}}-E-\overset{O}{\overset{\|}{C}}R$		$^{13}C{=}O$
R	E	δ	R	E	δ
2-$CH_3OC_6H_4$	O	163.9	2-$CH_3OC_6H_4$	O	162.7
	S	185.8		S	186.5
	Se	185.0		Se	189.4
	Te	177.8		Te	192.1

a) C_6D_6

References

1) S. Kato, Yuki Gosei Kagaku Kyokai Shi, 43, 660 (1985); S. Kato, T. Murai, and M. Ishida, Org. Prep. Proc. Int., 18, 369 (1986).

2) M. Ishida, T. Kakigano, and S. Kato, The 50th National Meeting of the Chemical Society of Japan, Tokyo, 1985 April, Abstr. II, p. 1210; S. Kato, T. Kakigano, and M. Ishida, Z. Chem., 26, 179 (1986). du Mont et al. reported at the same time the preparation of aliphatic bis(acyl) tellurides: T. Serengis, W. W. du Mont, D. Lenoir, and H. Voss, Angew. Chem., 97, 1051 (1985); Angew. Chem., Int. Ed. Engl., 24, 1041 (1985).

3) **1a**: Yield 86% mp 88 °C; IR (KBr) 1675, 1625 cm^{-1} (C=O); ^1H NMR (C_6D_6) $\delta=3.23$ (6H, s, CH_3O), 6.31-7.69 (8H, m, aromatic); ^{13}C NMR (C_6D_6) $\delta=55.7$ (CH_3), 112.7, 121.8, 129.0, 133.8, 134.4, 159.3 (aromatic), 192.1 (C=O); UV/Vis λ_{max} (CH_2Cl_2) 313, 350 sh, 400 sh, 460 sh; Found: C, 48.56; H, 3.67%: Calcd for $C_{16}H_{14}O_4Te$: C, 48.30; H, 3.55%.

4) **2a**: UV/Vis λ_{max} (CH_2Cl_2) 240, 270, 314, 360, 400 sh, 554 sh; ^1H NMR (d8-toluene) $\delta=0.87$-3.80 (10H, m, CH_2), 3.17 (3H, s, CH_3O), 6.23-7.09 (4H, m, aromatic), 7.85 (2H, br, $\overset{+}{N}H_2$). Ishihara et al. reported the preparation of piperidinium selenocarboxylates from the reaction of bis(acyl) selenide with piperidine: H. Ishihara and Y. Hirabayashi, Chem. Lett., 1976, 203. H. Ishihara, S. Sato, and Y. Hirabayashi, Bull. Chem. Soc. Jpn., 50, 3007 (1977).

5) **2b**: UV/Vis λ_{max} (CH_2Cl_2) 230, 270, 314, 360, 400 sh, 630 sh; ^1H NMR (d8-toluene) $\delta=2.63$-3.44 (8H, m, CH_2), 3.15 (3H, s, CH_3O), 6.20-7.30 (4H, m, aromatic), 8.18-8.4 (2H, br, $\overset{+}{N}H_2$).

6) **2c**: UV/Vis λ_{max} (CH_2Cl_2) 240, 275, 324, 390 sh, 554(?); ^1H NMR (d8-toluene) $\delta=$ 0.86-1.88 (10H, m, CH_2), 3.01 (3H, s, CH_3O), 3.49 (1H, m, CH), 6.20-8.50 (4H, m, aromatic), 8.43-8.68 (3H, br, $\overset{+}{N}H_3$).

7) **2d**: UV/Vis λ_{max} (CH_2Cl_2) 228, 250, 312, 400 sh, 547.

8) **3**: Mass m/z 280, 278, 276, 275, 274 (M^+).

9) **4**: Yield 32%; mp 108-110 °C (dec); IR (KBr) 1675, 1650 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) $\delta=4.15$ (3H, s, CH_3O), 7.00-8.90 (7H, m, aromatic); ^{13}C NMR ($CDCl_3$) $\delta=$ 56.3 (CH_3O), 112.1, 118.0, 120.1, 122.4, 127.7, 133.8, 136.3, 137.7, 144.0, 145.7, 159.9 (aromatic), 185.6 (C=O). Found: C, 36.40; H, 2.18; N, 6.06%. Calcd for $C_{14}H_{10}N_2O_6STe$: C, 36.23; H, 2.15; N, 6.21%.

10) **5a**: 52%; mp 130-131 °C (dec); IR (KBr) 1620 cm^{-1} (C=O); ^{13}C NMR (C_6D_6) $\delta=55.2$ (CH_3O), 112.5, 121.5, 127.7, 128.6, 134.7, 159.8 (aromatic), 177.8 (C=O); ^1H NMR (C_6D_6) $\delta=3.15$ (6H, s, CH_3O), 6.23-7.81 (8H, m, aromatic); UV/Vis λ_{max} (CH_2Cl_2) 253, 300 sh, 314, 403 sh, 480 sh; Found; C, 36.73; H, 2.66%. Calcd for $C_{16}H_{14}O_4Te_2$: C, 36.57; H, 2.69%.

11) Piperidinium dithiocarboxylates are readily oxidized by benzenesulfonyl chloride to give the corresponding bis(thioacyl) disulfide: S. Kato, T. Kato, T. Kataoka, and M. Mizuta, Int. J. Sulfur Chem., 8, 437 (1973).

12) **5b**: Yield 6%; mp 85-96 °C (dec); IR (KBr) 1655, 1620 cm^{-1}; ^{13}C NMR (C_6D_6) $\delta=$ 186.4 (C=O).

13) The pertelluro salt seems to be more labile than the telluro salt **2a**.

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