Tellurodicarbonic Acid Diesters; Preparation and Properties

Hitomi Suzuki* and Yoshinobu Nishioka
Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho, Matsuyama 790

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Synopsis. Title compounds were obtained as reasonably stable to labile oily substances by reacting alkyl carbonochloridates with sodium telluride under phase-transfer conditions at room temperature or in dry *N,N*-dimethylformamide under ice-cooling.

Tellurodicarbonic acid (**1**) is one of the tellurium isologues of dicarbonic acid, which has not hitherto been described in the literature. We now report the preparation of dialkyl 2-tellurodicarbonates (**2**) and their unique properties quite different from those of ordinary esters.

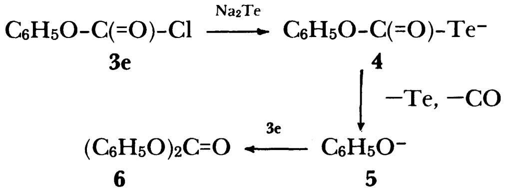
HO-C(=O)-Te-C(=O)-OH **1**

RO-C(=O)-Te-C(=O)-OR **2**

R	R
a: CH_3	d: $C_6H_5CH_2$
b: C_2H_5	e: C_6H_5
c: *i*-C_3H_7	

When a solution of alkyl carbonochloridates (**3**) in benzene was added slowly to an aqueous solution of sodium telluride in the presence of tetrabutylammonium bromide at room temperature, the initial reddish violet color gradually faded away and a yellow reaction mixture was obtained together with a small amount of free tellurium. After usual work-up followed by distillation of crude product under reduced pressure, compounds **2** were obtained as a pale yellow oil or low-melting colorless solid which, on standing in open air at room temperature, gradually got colored. Among four diesters **2a**—**2d** preparerd, diisopropyl ester **2c** is the most stable and can be stored for weeks without any appreciable change in a refrigerator. Dibenzyl ester **2d** is the most labile and begins to decompose within several hours after isolation, finally leading to a black resinous substance. Diesters **2** could be also obtained under aprotic conditions by reacting carbonochloridates **3** with sodium telluride in situ prepared from sodium hydride and tellurium in dry *N,N*-dimethylformamide (DMF). The yields of diesters usually ranged from 30 to 60%. Because of the instability of products under basic conditions employed, prolonged reaction time should be avoided.

Attempts to obtain diphenyl tellurodicarbonate (**2e**) under similar conditions were unsuccessful, however. The reaction with phenyl carbonochloridate (**3e**) went on smoothly, but the product isolated was not the expected dicarbonate **2e** but diphenyl carbonate (**6**). The initially formed phenyl tellurocarbonate anion (**4**) would readily collapse into phenolate ion (**5**), carbon monoxide and free tellurium, and the ion **5** thus formed would undergo further reaction with carbonochloridate **3e** to afford **6**.



3e **4** **6** **5**

Diesters **2** possess a characteristic odor not so offensive as that of lower dialkyl tellurides. On contact with skin, they produce black stains after a few hours,

Table 1. Dialkyl Tellurodicarbonates Prepared

Compound 2	R	Yield/%	Bp (°C/mmHg)[a] [Mp (°C)]	^{1}H NMR/δ	IR/cm^{-1}
2a	CH_3[b]	39	76/1.0	3.90 (s)	1720, 1420, 1180, 1065, 920, 790
2b	C_2H_5	48	89/1.5	1.36 (t, 6H; *J*=7 Hz), 4.37 (q, 4H; *J*=7 Hz)	1745,1690, 1440, 1380, 1070, 1000, 835, 800, 760
2c	*i*-C_3H_7[c]	69	99/1.0 [34—35]	1.33(d, 12H; *J*=7 Hz), 5.23 (sept, 2H; *J*=7 Hz)	1740, 1700, 1470, 1390, 1380, 1130, 1050, 900, 830
2d	$C_6H_5CH_2$[d]	50	163/1.0	5.24 (s, 4H), 6.9—7.2 (m, 10H)	1740, 1695, 1590, 1480, 1450, 1250, 1080, 1020, 750, 685

a) Boiling points refer to the Kugelrohr bath temperatures. b) Found: C, 19.35; H, 2.49%. Calcd for $C_4H_6O_4Te$: C, 19.55; H, 2.46%. c) Found: C, 31.52; H, 4.70%. Calcd for $C_8H_{14}O_4Te$: C, 31.84; H, 4.68%. d) Not analyzed due to rapid decomposition.

which persist for days. In marked contrast to ordinary esters, compounds **2** resist any further transformations but decomposition. Thus, attempted ester interchange with alcohols in the presence or absence of catalyst only resulted in the decomposition of diesters. Actions of sodium methoxide and diethylamine led to immediate and gradual decompositions of diesters, respectively. Reaction with excess of 4-methylphenylmagnesium bromide afforded bis(4-methylphenyl) ditelluride, which should have been formed by the reaction of the Grignard reagent with tellurium liberated from diester.

Tellurium(II) compounds bearing two carbonyl groups on the tellurium atom are known to be extremely unstable and easily decompose in open air.[1] Acyclic diacyl tellurides such as bis(2-chlorobenzoyl) telluride and di-1-naphthoyl telluride have only recently been isolated and characterized.[2] Thus it is worth mentioning here that diesters **2** in which two ester carbonyl groups attached geminally to the tellurium atom are much more stable toward oxidative degradation than diacyl tellurides.

Reaction of dimethylcarbamoyl chloride with sodium telluride under phase-transfer conditions did not lead to the expected tellurodicarbonic diamide but to bis(dimethylcarbamoyl) ditelluride in a low yield. The ditelluride is most likely to be derived from the oxidative coulpling of tellurocarbamate ion during work-up.[3,4]

Experimental

All melting and boiling points were uncorrected. Infrared spectra were measured as KBr pellets or as neat films between NaCl plates by using a Hitachi 260-10 photospectrometer and only prominent peaks between 2000 and 650 cm^{-1} are recorded. ^{1}H NMR spectra were determined on a Hitachi R-600 spectrometer using chloroform-*d* as solvent and TMS as internal standard. Mass spectra were obtained on a Hitachi M-80B spectrometer.

Preparation of Dialkyl Tellurodicarbonates: Typical Procedure; Method A: A mixture of tellurium (3.80 g; 30 mmol), Rongalite (9.2 g; 60 mmol) and 1 M (1 M=mol dm^{-3}) sodium hydroxide solution (180 mL) was stirred for 2 h at 60 °C under nitrogen to give sodium telluride as a wine-colored solution. After cooling an aqueous solution (5 mL) of tetrabutylammonium bromide (1.9 g; 6 mmol) followed by a solution of ethyl carbonochloridate (9.1 g; 84 mmol) in benzene (100 mL) was added dropwise with vigorous stirring. The initial color was lost within 15 min and small amounts of tellurium was liberated. The reaction mixture was then passed through a thin bed of Celite to remove the inorganic insolubles, the organic phase was separated, and dried over sodium sulfate. The solvent was evaporated under reduced pressure to leave diester **2b** as a pale yellow oil, which was further purified by Kugelrohr distillation. Bp 89 °C/1.0 mmHg (1 mmHg≈133.322 Pa). Yield, 3.9 g (48%). MS (20 eV): *m/z* (relative intensity) 274 (M$^+$, 4.4), 232 (7.0), 204 (95.3), 176 (100), 159 (38.7), 130 (71.6), and 73 (20.5). Found: C, 26.21; H, 3.69%. Calcd for $C_6H_{10}O_4Te$: C, 26.31; H, 3.68%.

Method B: A mixture of sodium hydride (53 mg; 2.2 mmol; washed thoroughly with hexane prior to use), tellurium (128 mg; 1 mmol) and dry DMF (1 mL) was heated at 120 ° C for 1 h under nitrogen to give sodium telluride as a pale yellow suspension. After cooling to room temperature, ethyl carbonochloridate (325 mg; 3.0 mmol) in the same solvent (1 mL) was added dropwise. The mixture turned reddish brown under evolution of white fumes. After 15 min the reaction was quenched by the addition of water and the organic phase was extracted with benzene. The extract was washed with water, filtered through a thin bed of Celite, dried over sodium sulfate, and evaporated in vacuo to leave an oil, which was purified by bulb-tobulb distillation to give diester **2b** in 47% yield.

Reaction of Phenyl Carbonochloridate (3e) with Sodium Telluride: To a wine-colored solution of sodium telluride prepared from tellurium (128 mg; 1.0 mmol), Rongalite (310 mg; 2 mmol) and 1 M sodium hydroxide solution (6 mL) was added an aqueous solution (1 mL) of tetrabutylammonium bromide (64 mg; 0.2 mmol) followed by a solution of phenyl carbonochloridate (330 mg; 2 mmol) in benzene (5 mL) under nitrogen at room temperature. Within 15 min the initial color was lost under the separation of free tellurium. The resulting mixture was passed through a thin bed of Celite to remove the insolubles and the product was extracted with benzene. The extract was dried with sodium sulfate and evaporated under reduced pressure to leave a solid, which was crystallized from hexane to give diphenyl carbonate **6** as white crystals, mp 77—78 °c (lit,[5] 78 °C). Yield, 174 mg (77% based on carbonochloridate).

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