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Synthesis of Te-Alkyl Carbamotelluroates from Tellurium, Carbon Monoxide, Amines, and Alkyl Halides

Toru Inoue, Toshiaki Mogami, Nobuaki Kambe,* Akiya Ogawa, and Noboru Sonoda*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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ABSTRACT

Lithium amides reacted with tellurium under atmospheric pressure of carbon monoxide to yield lithium carbamotelluroates which were trapped with alkyl halides to give Te-alkyl carbamotelluroates in good yields. Results of control experiments suggested that lithium carbamotelluroates were formed by the reaction of tellurium with carbamoyllithiums generated in situ from lithium amides and carbon monoxide. It was revealed also that yields were improved when tellurium was preliminarily treated with lithium amides prior to the introduction of carbon monoxide into the reaction media.

Carbamoyllithiums are attractive reagents for nucleophilic introduction of carbamoyl moieties into organic molecules [1]. Their synthetic utility has been demonstrated clearly by our recent study which achieved efficient generation of carbamoyllithiums from carbamotelluroates by lithium-tellurium exchange reactions and their successful trapping with a variety of electrophiles [1b]. In order to make this transformation practically useful for organic synthesis, general and convenient synthetic methods of carbamotelluroates are strongly demanded. The hitherto known methods for their preparation are limited only to the substitution of carbamoyl chlorides with tellurolates [1b] and telluration of N,N-dimethylformamide [2]. As for the selenium analogues, Se-alkyl carbamoselenoates were obtained in good yields by the alkylation with alkyl halides of ammonium carbamoselenoates generated in situ from selenium, carbon monoxide, and secondary amines [3]. This reaction can be carried out conveniently at room temperature under atmospheric pressure of carbon monoxide. These successful results led us to examine the reaction of tellurium with carbon monoxide and amines under similar conditions, but no reaction took place and tellurium was recovered unchanged. Since this may be due to the low reactivity of tellurium, we then employed lithium amides instead of amines and found that tellurium reacts with lithium amides and carbon monoxide at low temperatures to form lithium carbamotelluroates which undergo alkylation with alkyl halides to yield Te-alkyl carbamotelluroates.

A typical example is as follows. To a flame-dried, 30 mL, three-necked, round bottom flask equipped with an Ar inlet, a CO inlet, and a rubber septum, 10 mL of THF and 5 mmol of piperidine were placed under Ar. The solution was cooled to −78°C, and 5.5 mmol of ^{n}BuLi (1.6 N in hexane) was injected with stirring. After 15 minutes, finely ground elemental tellurium (638 mg, 5 mmol) was added and the mixture was allowed to warm to 10°C. All of the tellurium pieces disappeared within 1 hour to give a dark violet homogeneous solution. The solution was cooled to −78°C again, purged with carbon monoxide, and stirred for 2 hours, resulting in the absorption of 129 mL (5.8 mmol) of carbon monoxide. At this stage, lithium piperidi-

*Dedicated to Prof. Antonino Fava on the occasion of his seventieth birthday.

To whom correspondence should be addressed.

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necarbamotelluroate (**1a**) was expected to be formed (vide infra). Into the solution, 5.5 mmol of EtBr was added and the mixture was warmed to 10°C and stirred for another 30 minutes. Products were extracted with Et_2O, dried over $MgSO_4$, and concentrated. By column chromatography (silica gel, pentane/Et_2O = 9/1), Te-ethyl 1-piperidinecarbotelluroate (**2a**) was isolated in 65% yield based on the tellurium used (Equation 1).

In a similar manner, several Te-alkyl carbamotelluroates were prepared by use of secondary amines and alkyl halides (Table 1). In contrast to the results with dialkylamines, which afforded desired products in satisfactory yields under the conditions described above (runs 1–7), amines carrying a phenyl substituent gave only a small amount of carbamotelluroates under the same conditions, resulting in the recovery of metallic tellurium. This may be due to the lower reactivity of lithium anilides in comparison to lithium dialkylamides. Actually, corresponding carbamotelluroates were obtained in moderate yields when all steps of the reaction were performed at 10°C (runs 8 and 9).

The evidence that Te-alkyl carbamotelluroates were obtained by the addition of alkyl halides at the final step of the reaction indicates that lithium carbamotelluroates were formed as the intermediates from tellurium, lithium amides, and carbon monoxide. We then examined the reaction pathway of the formation of lithium carbamotelluroates. The most straightforward pathway is the reaction of tellurium with carbamoyllithiums generated in situ by the reaction of lithium amides with carbon monoxide (Path A). But contrary to expectation, when tellurium powder was added to the THF solution of a carbamoyllithium (**3a**) prepared by the reaction of carbon monoxide with lithium piperidide, only 12% of the desired product (**2b**) was obtained along with a 25% yield of **4** (Equation 2). This yield is much lower than that achieved by the procedure mentioned earlier. This is in large contrast with the case of sulfur which affords lithium carbamothioates by the reaction of elemental sulfur with carbamoyllithiums in good yields [1a]. These results led us to propose an alternative pathway (Path B), where tellurium reacts with lithium amides to form **5** which then reacts with carbon monoxide to give lithium carbamotelluroates (**1**) via rearrangement of transiently formed intermediates (**6**). These pathways are shown in Scheme 1. In order to evaluate the probabilities of these pathways, *i.e.*, with which substrates lithium amides react first, carbon monoxide (Path A) or tellurium (Path B), the following two control experiments were performed. Into the THF solutions of carbamoyllithiums prepared separately from lithium 4-methylpiperidide and lithium piperidide were added the homogeneous solutions obtained by the reaction of tellurium with lithium piperidide and with lithium 4-methylpiperidide, respectively. Quenching of these reactions with ethyl bromide gave Te-ethyl carbamotelluroates derived from carbamoyllithiums as the major products in both cases (Equations 3 and 4).

These results indicate that Path A seems more plausible. The fact that a carbamotelluroate (**2b**) was obtained in a poor yield when lithium piperidide was allowed to react with carbon monoxide

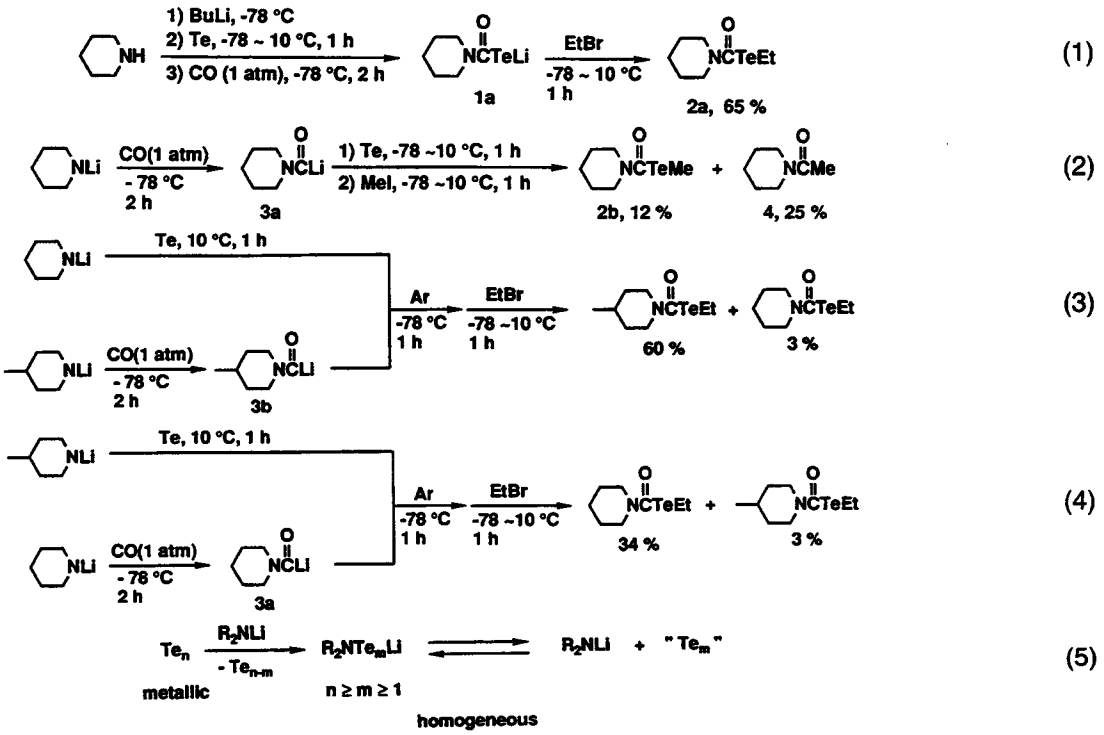
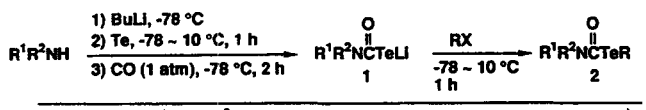


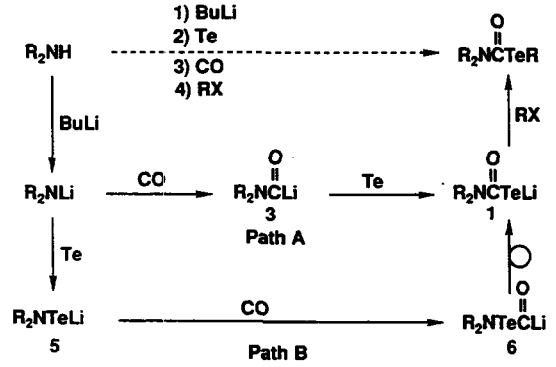
TABLE 1 Formation of Te-Alkyl Carbamotelluroates



run	R^1	R^2	RX	product		yield, %[a]
1	$-(CH_2)_3-$		EtBr	NCTeEt	2a	65
2	$-(CH_2)_3-$		MeI	NCTeMe	2b	61
3	$-(CH_2)_3-$		^{n}PrBr	NCTePr^n	2c	41
4	$-(CH_2)_3-$		^{n}BuI	NCTeBu^n	2d	62
5	$-(CH_2)_3-$		$PhCH_2Br$	NCTeCH$_2$Ph	2e	67
6	$-CH_2CH_2CHMeCH_2CH_2-$		EtBr	NCTeEt	2f	62
7	Me	Me	EtBr	NCTeEt (Me, Me)	2g	48
8[b]	Ph	Me	EtBr	NCTeEt (Ph, Me)	2h	43
9[b]	Ph	$PhCH_2$	EtBr	NCTeEt (Ph, $PhCH_2$)	2i	31

a) Isolated yield based on tellurium used.
b) Reaction was carried out at 10°C all through.

prior to the addition of tellurium (Equation 2) may be explained by the supposition that carbamoyllithium (**3a**) is kinetically somewhat unstable and does not react efficiently with metallic tellurium. Rautenstrauch and Joyeux have reported a complex result obtained by the reaction of lithium piperidide with CO followed by quenching with methyl iodide, where a 33% yield of an amide (**4**) was obtained along with α-oxopropionamide as a by-product [4]. When tellurium powder was added to lithium amides in THF at 10°C, the mixture turned to a dark violet homogeneous solution [5] in a few minutes. We assume that lithium amides attack metallic tellurium to form R_2NTe_mLi. This species may be present in an equilibrium with R_2NLi and "Te_m" in solution, which reacts with carbamoyllithiums much faster than metallic tellurium to give lithium carbamotelluroates. Although the formation of R_2NTe_mLi and "Te_m" has not been confirmed, the reaction expressed by Equation 5 would well account for the better yields achieved when tellurium was allowed to react with lithium amides prior to the introduction of carbon monoxide into the reaction media. Lower yields of products in the cases of aromatic amines may arise from the relatively low nucleophilicity and/or higher thermodynamic stability of the anilide anions. Actually, metallic tellurium did not afford completely homogeneous solutions by the treatment with lithium anilides, and some of the tellurium powder remained unchanged. We have also revealed separately that a carbamoyllithium having an aromatic substituent on nitrogen easily releases carbon monoxide [6].



SCHEME 1

EXPERIMENTAL

Instruments and Materials

THF was distilled from sodium benzophenone ketyl. Amines and alkyl halides were dried with CaH_2 and fractionally distilled before use. Tellurium was ground with a mortar and pestle just before use. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-270 spectrometer using $CDCl_3$ as a solvent with Me_4Si as an internal standard. IR spectra were obtained on a Perkin-Elmer Model 1600 spectrometer. Mass spectra were measured on a Hitachi Model RMU-6E instrument. Melting points (uncorrected) were determined by using a Yanagimoto micromelting point apparatus. Elemental analyses were performed on a Yanagimoto CHN-Corder MT-2 instrument.

Te-ethyl 1-Piperidinecarbotelluroate (**2a**). ^1H NMR (270 MHz, $CDCl_3$) δ 1.40–1.70 (m, 9H), 2.75–2.90 (m, 2H), 3.00–3.14 (m, 2H), 3.50–3.64 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 4.1, 17.5, 24.4, 25.1, 25.9, 44.0, 49.0, 153.1; IR (neat) 1627, 1388, 1232, 1189, 1107, 989 cm^{-1}; MS *m/e* (relative intensity) 271 (M^+, 5.8), 157 (2.8), 112 (100), 84 (4.3). Anal. calcd for $C_8H_{15}NOTe$: C, 40.50; H, 6.45; N, 4.72. Found: C, 40.63; H 6.59; N, 4.60.

Te-methyl 1-Piperidinecarbotelluroate (**2b**). ^1H NMR (270 MHz, $CDCl_3$) δ 1.45–1.73 (m, 6H), 2.06–2.15 (m, 3H), 3.06–3.27 (m, 2H), 3.55–3.74 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 12.6, 24.0, 24.7, 25.5,

44.2, 48.6, 152.2; IR (neat) 1645, 1399, 1206, 1116 cm^{-1}; MS *m/e* (relative intensity) 257 (M^+, 3.5), 145 (5.0), 130 (2.1), 112 (100), 84 (3.9). Anal. calcd for $C_7H_{13}NOTe$: C, 35.75; H, 5.62; N, 5.21. Found: C, 35.66; H, 6.59; N, 5.30.

Te-propyl 1-Piperidinecarbotelluroate (**2c**). ^1H NMR (270 MHz, $CDCl_3$) δ 0.99 (t, J = 7.3 Hz, 3H), 1.48–1.75 (m, 6H), 1.85 (sextet, J = 7.3 Hz, 2H), 2.93 (t, J = 7.3 Hz, 2H), 3.07–3.24 (m, 2H), 3.56–3.73 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.9, 16.6, 24.8, 25.3, 25.4, 26.2, 44.8, 49.4, 153.7; IR (neat) 1638, 1399, 1206, 1116 cm^{-1}; MS *m/e* (relative intensity) 285 (M^+, 4), 173 (1.3), 130 (0.9), 112 (100), 84 (4), 69 (64), 41 (37). Anal. calcd for $C_9H_{17}NOTe$: C, 38.22; H, 6.06; N, 4.95. Found: C, 38.38; H, 6.19; N, 4.89.

Te-butyl 1-Piperidinecarbotelluroate (**2d**). ^1H NMR (270 MHz, $CDCl_3$) δ 0.96 (t, J = 7.3 Hz, 3H), 1.44 (sextet, J = 7.3 Hz, 2H), 1.50–1.77 (m, 6H), 1.86 (quint, J = 7.3 Hz, 2H), 2.97 (t, J = 7.3 Hz, 2H), 3.18 (m, 2H), 3.68 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 12.1, 13.1, 24.7, 25.1, 25.3, 26.1, 34.0, 44.7, 49.3, 153.4; IR (neat) 1660, 1411, 1218, 1130, 800, 780 cm^{-1} MS *m/e* (relative intensity) 299 (M^+, 1.5), 187 (0.5), 112 (100), 84 (2.8), 57 (7.2). Anal. calcd for $C_{10}H_{19}NOTe$: C, 40.50; H, 6.45; N, 4.72. Found: C, 40.63; H, 6.59; N, 4.60.

Te-benzyl 1-Piperidinecarbotelluroate (**2e**). ^1H NMR (270 MHz, $CDCl_3$) δ 1.49–1.73 (m, 6H), 3.06 (m, 2H), 3.67 (m, 2H), 4.37 (s, 2H), 7.08–7.41 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 15.3, 24.5, 25.3, 26.0, 44.9, 49.3, 125.8, 128.2, 128.3, 141.4, 154.5; IR (KBr) 1628, 1401, 1205, 1111, 993 cm^{-1}; MS *m/e* (relative intensity) 333 (M^+, 2.8), 221 (0.6), 112 (100), 91 (35), 84 (3.0). Anal. calcd for $C_{13}H_{17}NOTe$: C, 47.19; H, 5.18; N, 4.23. Found: C, 47.06; H, 5.16; N, 4.22; mp 53.6–54.1°C.

Te-ethyl 4-Methyl-1-piperidinecarbamotelluroate (**2f**). ^1H NMR (270 MHz, $CDCl_3$) δ 0.91 (d, J = 7.6 Hz, 3H), 0.96–1.18 (m, 2H), 1.50–1.70 (m, 6H), 2.62–2.78 (m, 1H), 2.83 (q, J = 7.6 Hz, 2H), 2.88–3.03 (m, 1H), 3.14–3.29 (m, 1H), 4.40–4.54 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 3.8, 17.0, 20.7, 30.6, 32.8, 33.5, 43.2, 47.9, 152.7; IR (neat) 1642, 1401, 1195, 1119, 956 cm^{-1}; MS *m/e* (relative intensity) 285 (M^+, 0.2), 126 (100), 98 (91). Anal. calcd for $C_9H_{17}NOTe$: C, 38.22; H, 6.06; N, 4.95. Found: C, 38.40; H, 6.18; N, 5.10.

Te-ethyl N,N-Dimethylcarbamotelluroate (**2g**). ^1H NMR (270 MHz, $CDCl_3$) δ 1.79 (t, J = 7.3 Hz, 3H), 2.96 (s, 3H), 2.99 (q, J = 7.3 Hz, 2H), 3.14 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 4.9, 17.8, 35.6, 38.4, 156.1; IR (neat) 1640, 1357, 1253, 1081 cm^{-1}; MS *m/e* (relative intensity) 231 (M^+, 5.2), 159 (2.0), 130 (1.3), 72 (100), 44 (2.5). Anal. calcd for $C_5H_{11}NOTe$: C, 26.25; H, 4.85; N, 6.12. Found: C, 26.23; H, 4.95; N, 6.12.

Te-ethyl N-Methyl-N-phenylcarbamotelluroate (**2h**). ^1H NMR (270 MHz, $CDCl_3$) δ 1.73 (t, J = 7.6 Hz, 3H), 2.84 (q, J = 7.6 Hz, 2H), 3.42 (s, 3H), 7.34–7.50 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 4.8, 17.4, 36.8, 128.7, 128.8, 129.2, 142.0, 156.7; IR (nujol) 1660, 1452, 1376, 1258 cm^{-1}; MS *m/e* (relative intensity) 293 (M^+, 4.6), 157 (1.3), 130 (100), 106 (38), 77 (30). Anal. calcd for $C_{10}H_{13}NOTe$: C, 41.30; H, 4.51; N, 4.82. Found: C, 41.30; H, 4.52; N, 4.78; mp 48.1–49.0°C.

Te-ethyl N-Benzyl-N-phenylcarbamotelluroate (**2i**). ^1H NMR (270 MHz, $CDCl_3$) δ 1.67 (t, J = 7.6 Hz, 3H), 2.79 (q, J = 7.6 Hz, 2H), 4.93 (s, 2H), 7.06–7.36 (m, 10H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 5.3, 17.5, 53.5, 118.6, 122.9, 128.7, 129.2, 129.6, 139.6, 140.6, 157.5; IR (neat) 1647, 1462, 1372, 1241 cm^{-1}; MS *m/e* (relative intensity) 369 (M^+, 2), 210 (14), 182 (3), 91 (100), 77 (3); HRMS calcd for $C_{16}H_{17}NOTe$ 369.0372, found 369.0366.

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[5] This can be a suspension. If so, tellurium must be atomic or consist of very fine particles since no deposition of tellurium was observed on standing.

[6] Details will be reported in due course.