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A Convenient Synthesis of Unsymmetrical Tellurides by a Sequential Reductive Cleavage of Bis(N,N-dimethylcarbamoyl) Ditelluride

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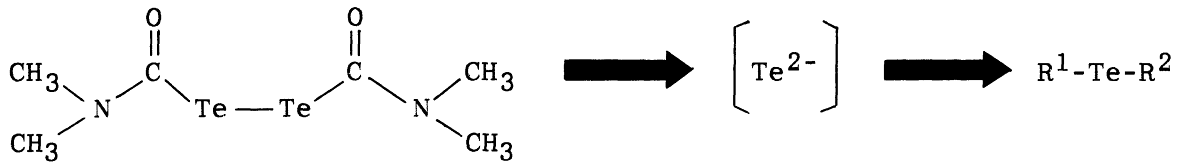
Bis(N,N-dimethylcarbamoyl) ditelluride was converted to unsymmetrical tellurides possessing various substituents by a convenient stepwise reduction-alkylation or reduction-addition sequence.

Recently in the field of organic heteroatom chemistry, interest in the structure and synthesis of organotellurium compounds has been growing rapidly.$^{1-7)}$ However, in spite of the considerable needs for the preparation of unsymmetrical tellurides related to novel tellurocarbonyl compounds,$^{8-11)}$ the low stability of the precursors and reagents has impeded development of a variety of methods of unsymmetrical alkenyl tellurides. It has been assumed that formal unsymmetrical alkylation of Te^{2-} would be realized by the regioselective Te-Te bond cleavage of polytellurides possessing non-metallic protecting groups on both terminals. In respect of air-stability and solubility in organic solvents, bis(N,N-dialkylcarbamoyl) ditelluride 1 is expected to behave as a new synthetic equivalent of unsymmetrical Te^{2-} anion and vinyl tellurolate anions by the selective conversion in which reductive cleavage of the Te-Te bond and removal of the carbamoyl groups are combined. In this paper we would like to describe a convenient preparation of tellurides possessing various substituents by applying a novel stepwise reduction-alkylation or reduction-addition sequence to bis(N,N-dimethylcarbamoyl) ditelluride 1.$^{12)}$



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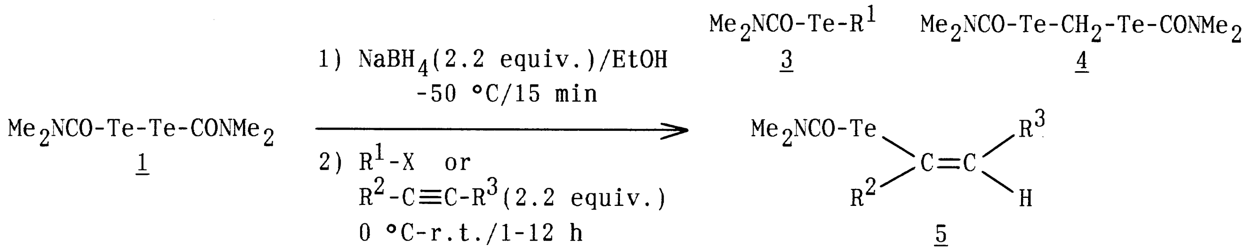
Bis(N,N-dimethylcarbamoyl) ditelluride 1 was prepared in 58% yield by treating DMF with sodium metal and elemental tellurium under Ar atmosphere according to Suzuki's method.$^{12)}$ Reductive Te-Te bond cleavage of 1 was carried out by treating 1 with 2 equiv. of $NaBH_4$ in EtOH-DMF at -50 °C to generate anion 2, and subsequent addition of various alkyl halides to the reaction mixture afforded tellurocarbamates 3 in good yields. A telluroacetal 4 and alkenyl tellurocarbamates 5 were also obtained in high yields by treating anion 2 with CH_2Br_2 and substituted acetylenes in a similar manner. However, phenylacetylene was not reactive to the nucleophilic addition of anion 2. Physical properties of the products including MS, IR, and ^1H NMR were fully consistent with the structure of the products.[13] Z-Geometry of the alkenyl groups was also assigned by the coupling constants of olefinic vicinal protons revealed in ^1H NMR spectra. Table 1 shows all results of the reactions.

Table 1. Synthesis of tellurocarbamates 3, 4, and 5 by the stepwise treatment of ditelluride 1 with $NaBH_4$ and electrophilic reagents



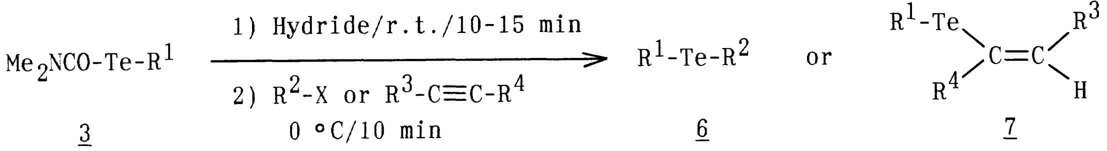
R^1-X	Product	Yield[a] %	Acetylene R^2	R^3	Product	Yield %
CH_3I	3a	87	H	CO_2CH_3	5a	88
$C_6H_{13}I$	3b	92	CH_3	CO_2CH_3	5b	61
$C_8H_{17}Cl$	3c	63	C_6H_5	CO_2CH_3	5c	70
c-$C_6H_{11}I$	3d	26	H	C_6H_5	5d	24[a]
$C_6H_5CH_2Br$	3e	92				
CH_2=$CHCH_2Br$	3f	89				
CH_2Br_2	4	68				

a) Refluxing in EtOH for 3 hours.

Compounds 3 were treated with $NaBH_4$ in EtOH at refluxing temperature or $LiAlH_4$ in Et_2O at room temperature followed by the treatment of various electrophilic reagents such as alkyl halides and substituted acetylenes to give unsymmetrical tellurides 6, 7, and 8 in high to modest yields. Physical properties of products 6, 7, and 8 were also fully consistent with their structure including MS, IR, and ^1H NMR.[14] All results are shown in Table 2 and Table 3. In all cases, the geometry of the double bonds in 7 was Z, as was reported in nucleophilic addition of thiols and thiolate anions to acetylenes.[15] Furthermore, it was noteworthy that stepwise reduction-alkylation of alkenyl tellurocarbamates was effective for the synthesis of unsymmetrical dialkenyl tellurides. Interestingly, the geometry of the double bonds in the starting alkenyl tellurocarbamates was completely retained in the alkenyltellurolate anions under these reaction conditions.

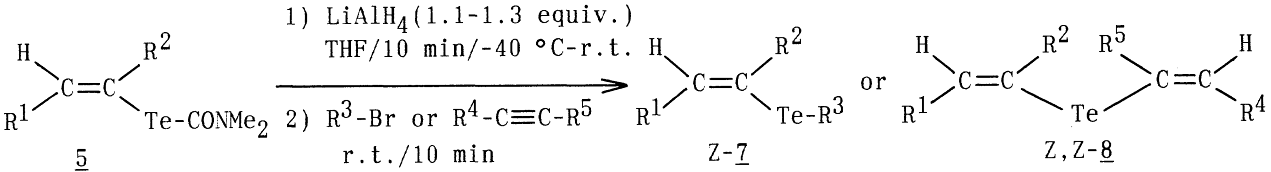
Conclusively, a convenient synthesis of unsymmetrical tellurides was achieved by the use of repeated stepwise reduction-alkylation sequence starting from bis(N,N-dimethylcarbamoyl) ditelluride 1. This procedure is substantially based on the different reactivities of Te-Te and C-Te bonds on compound 1 toward the attack of hydrides. Alkenyl tellurides, dialkenyl tellurides, and a telluroacetal related to tellurocarbonyl compounds were also synthesized by using this sequence. Further conversion of these products to the novel tellurocarbonyl compounds is now in progress in our laboratory.

Table 2. Synthesis of unsymmetrical tellurides 6 and 7



R^1	Hydride(equiv.)	Solvent	Reagent			Product	Yield
			R^2-X	R^3	R^4		%
C_8H_{17}	$LiAlH_4$(1.1)	THF	CH_3I			6a	97
c-C_6H_{11}	$LiAlH_4$(1.1)	THF	CH_3I			6b	84
C_6H_{13}	$LiAlH_4$(1.1)	THF	C_6H_5COCl			6c	93
C_6H_{13}	$NaBH_4$(1.6)	EtOH		C_6H_5	H	7a	91
CH_2=$CHCH_2$	$LiAlH_4$(1.1)	THF		CO_2CH_3	H	7b	64
CH_2=$CHCH_2$	$LiAlH_4$(1.1)	THF		CO_2CH_3	C_6H_5	7c	47

Table 3. Synthesis of allyl alkenyl tellurides 7 and dialkenyl tellurides 8



Substrate		Reagent			Product	Yield
R^1	R^2	R^3	R^4	R^5		%
CO_2CH_3	H	CH_2=$CHCH_2$			7b	22
CO_2CH_3	C_6H_5	CH_2=$CHCH_2$			7c	64
CO_2CH_3	CH_3	CH_2=$CHCH_2$			7d	73
CO_2CH_3	CH_3	(E)-C_6H_5-CH=$CHCH_2$			7e	74
C_6H_5	H	CH_2=$CHCH_2$			7f	83
CO_2CH_3	C_6H_5		CO_2CH_3	H	8a	72
C_6H_5	H		CO_2CH_3	H	8b	65

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13) Physical data of tellurocarbamates. 4: Colorless needles, mp 80.5-81.5 °C; MS(m/e) 418 (M^+,33%,^{130}Te), 270(CH_2Te_2,bp,^{130}Te); IR(KBr) 1640, 1355, 1250, 1070, 880, 670 cm^{-1}; ^1H NMR($CDCl_3$): δ 2.85(6H,s), 3.10(6H,s), 3.90(2H,s). 5a: Colorless needles; mp 104.0-105.0 °C; MS(m/e) 287(M^+,bp,^{130}Te); IR(KBr) 1690, 1630, 1560, 1320, 1205 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.96(3H,s), 3.09(3H,s), 3.80(3H,s), 6.95(1H,d,J=10 Hz), 8.94(1H,d,J=10 Hz). 5b: Yellow oil; MS(m/e) 301(M^+,11%,^{130}Te), 72(bp); IR(neat) 1685, 1639, 1579, 1436, 1353, 1324, 1204, 1082, 1043, 880, 837 cm^{-1}; ^1H NMR($CDCl_3$): δ 2.63(3H,d,J=1 Hz), 3.06 (6H,s), 3.75(3H,s), 6.59(1H,q,J=1 Hz). 5c: Yellow oil; MS(m/e) 363(M^+,2%,^{130}Te), 72 (bp); IR(neat) 1620, 1560, 1435, 1310, 1170, 1080, 1010, 960, 840, 760, 720, 690, 660 cm^{-1}; ^1H NMR($CDCl_3$): δ 2.65(3H,br.s), 2.79(3H,br.s), 3.81(3H,s), 6.72(1H,s), 7.25-7.50(5H,m). 5d: Yellow plates, mp 46.0-47.0 °C; MS(m/e) 305(M^+,23%,^{130}Te), 103(bp); IR(neat) 1653, 1442, 1358, 1240, 1082, 878, 777, 661 cm^{-1}; ^1H NMR($CDCl_3$): δ 2.89(3H, s), 3.09(3H,s), 7.26(1H,d,J=10 Hz), 7.25-7.40(5H,m), 7.48(1H,d,J=10 Hz).

14) Physical data of alkenyl tellurides. 7b: Pale yellow oil; MS(m/e) 256(M^+,10%,^{130}Te), 215(bp); IR(neat) 1680, 1530, 1330, 1200 cm^{-1}; ^1H NMR($CDCl_3$): δ 3.30(2H,d,J=7.5 Hz), 3.78(3H,s), 4.86(1H,d,J=7.5 Hz), 5.01(1H,d,J=16 Hz), 6.01(1H,ddt,J=16,10,8 Hz), 6.95 (1H,d,J=10 Hz), 8.54(1H,d,J=10 Hz). 7c: Yellow oil; MS(m/e) 332(M^+,4%,^{130}Te), 15(bp); IR(neat) 1680, 1560, 1435, 1310, 1180, 1020, 900, 840, 770, 700, 600 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.85(2H,d,J=7.5 Hz), 3.80(3H,s), 4.72(1H,d,J=18 Hz), 4.75(1H,d,J=11 Hz), 5.48-5.95(1H,m), 6.65(1H,s), 7.25-7.50(5H,m). 7d: Pale yellow needles, mp 47.5-48.5 °C; MS(m/e) 270(M^+,26%,^{130}Te), 225(bp); IR(KBr) 1665, 1570, 1439, 1320, 1203, 1185, 1041, 902, 842 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.41(3H,d,J=1 Hz), 3.42(2H,d,J=7 Hz), 3.73(3H, s), 4.88(1H,br.d,J=10 Hz), 5.05(1H,br.d,J=16 Hz), 6.02(1H,ddt,J=16,10,8 Hz), 6.57(1H, q,J=1 Hz). 7e: Pale yellow needles, mp 81.5-82.5 °C; MS(m/e) 346(M^+,2%,^{130}Te), 117(bp); IR(KBr) 1680, 1575, 1436, 1329, 1202, 956, 825, 794, 693 cm^{-1}; ^1H NMR($CDCl_3$): δ 2.46(3H,d,J=1 Hz), 3.62(2H,dd,J=5,2 Hz), 3.73(3H,s), 6.34-6.47(2H,m), 6.58(1H,q,J=1 Hz), 7.18-7.35(5H,m). 7f: Yellow oil; MS(m/e) 274(M^+,64%,^{130}Te), 231(bp); IR(neat) 1626, 1598, 1491, 1443, 1330, 1134, 985, 771, 699 cm^{-1}; ^1H NMR($CDCl_3$): δ 3.42(2H,d,J=7 Hz), 4.89(1H,d,J=10 Hz), 5.02(1H,d,J=16 Hz), 6.03(1H,ddt,J=16,10,8 Hz), 6.87(1H,d,J=10 Hz), 7.05-7.50(5H,m), 7.40(1H,d,J=10 Hz). 8a: Yellow needles, mp 97.0-98.0 °C; MS(m/e) 376(M^+,25%,^{130}Te), 161(bp); IR(KBr) 1680, 1561, 1433, 1323, 1215, 1175, 1008, 863, 808, 696 cm^{-1}; ^1H NMR($CDCl_3$): δ 3.73(3H,s), 3.78(3H,s), 6.60(1H,d,J=11 Hz), 6.62 (1H,s), 7.10(5H,m), 7.70(1H,d,J=11 Hz). 8b: Pale yellow oil; MS(m/e) 318(M^+,36%, ^{130}Te), 129(bp); IR(neat) 1682, 1558, 1435, 1344, 1216, 1005, 805, 772, 701 cm^{-1}; ^1H NMR($CDCl_3$): δ 3.76(3H,s), 6.92(1H,d,J=10 Hz), 7.12(1H,d,J=11 Hz), 7.15-7.50(5H,m), 7.48(1H,d,J=11 Hz), 8.40(1H,d,J=10 Hz).

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