Unusual reactions of 2-methyltellurocyclohexene-1-carbaldehyde with phenacyl bromides

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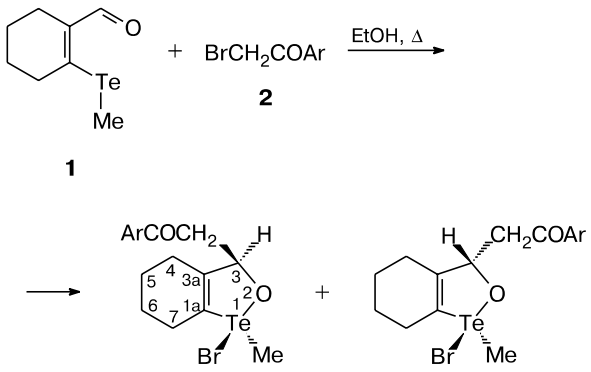
Reactions of dialkyl and alkyl aryl tellurides R^1R^2Te (R^1 and R^2 = Alk; R^1 = Alk, R^2 = Ar) with phenacyl bromides in the molar ratio 1 : 1 usually yield telluronium salts $R^1R^2(ArCOCH_2)Te^+Br^-$ **1** (X-ray diffraction data[2]). Divinyl telluride $(CH_2{=}CH)_2Te$ reacts with alkyl iodides to give divinylalkyltelluronium salts $(CH_2{=}CH)_2AlkTe^+I^-$.[3] Reactions of 2-methyltellurocyclohexene-1-carbaldehyde (**1**)[4,5] with phenacyl bromides **2** occur in an absolutely different fashion. Heating of an equimolar mixture of these reagents in boiling ethanol gave earlier unknown 3-aroylmethyl-1-bromo-1-methyl-1,3,4,5,6,7-hexahydro-2,1λ⁴-benzoxatelluroles (**3**) in 45—60% yields. The reaction rate is determined by the nature of the *p*-substituent in the arene ring of phenacyl bromide, decreasing in the order NO_2 > H > OMe. The ^1H, ^{13}C, and ^{125}Te NMR spectra of heterocycles **3** suggest that they are composed of two diastereomers.



Ar = Ph (**a**), 4-$NO_2C_6H_4$ (**b**), 4-$MeOC_6H_4$ (**c**)

The structures of the compounds obtained were proven by ^1H, ^{13}C, and ^{125}Te NMR spectroscopy and confirmed by elemental analysis. The ^1H NMR spectra of compounds **3** show two multiplets for the methine protons at δ 5.27—5.76 and four quartets for the methylene protons at δ 2.95—3.44, which correspond to two diastereomers of heterocycle **3**. The ^{13}C NMR spectrum of oxatellurole **3a** contains two singlet signals for the carbonyl C atom at δ 197.2 and 197.7 (in the starting compound **1**, a signal for the aldehyde C atom appears at δ 192.0). The ^{125}Te NMR spectrum of oxatellurole **3a** shows two singlets at δ 1177.8 and 1179.5, while a singlet in the ^{125}Te NMR spectrum of aldehyde **1** is observed at δ 537.7.

The integral intensities of the signals for the methylene and methine protons indicate that the content of one of the diastereomers increases with strengthening of the electron-withdrawing properties of the *para*-substituent in the arene ring. For instance, the ratio of the diastereomers was 31 : 69 (**3c**, R = OMe), 65 : 35 (**3a**, R = H), and 87 : 13 (**3b**, R = NO_2).

Compounds **3** are first representatives of oxatelluroles with a four-coordinate tellurium atom, which contain functional groups in position 3 of the heterocycle. Earlier,[6] 2-aryl-2-chloro-5*H*-[2,1]oxatelluroles with a hydrogen atom or an aryl radical in this position have been reported.

According to X-ray diffraction data,[7] 2-methyltellurocyclohexene-1-carbaldehyde is stabilized by an intramolecular O→Te coordination bond; its length (2.692 Å) is shorter by nearly 0.9 Å than the sum of the van der Waals radii of these atoms (3.60 Å).[8] This bond, as well as the high halophilicity of tellurides **1**, are probably responsible for the unusual pathway of the title reaction.

^1H, ^{13}C, and ^{125}Te NMR spectra were recorded on a Varian Unity-300 spectrometer.

The synthesis of oxatelluroles **3** was illustrated with compound **3a**.

3-Benzoylmethyl-1-bromo-1-methyl-1,3,4,5,6,7-hexahydro-2,1λ⁴-benzoxatellurole (3a). A solution of 2-methyltellurocyclohexene-1-carbaldehyde (1.0 g, 3.97 mmol) and phenacyl bromide (**2a**) (0.80 g, 3.97 mmol) in ethanol (20 mL) was refluxed for 40 min until a precipitate began to form. The reaction mixture was cooled and the precipitate was filtered off and dried. The yield of compound **3a** was 0.93 g (52%), colorless crystals, m.p. 161—162 °C (from chloroform—methanol (1 : 3)). Found (%): C, 42.41; H, 4.15. $C_{16}H_{19}BrO_2Te$. Calculated (%): C, 42.62; H, 4.26.

^1H NMR ($CDCl_3$), δ: 1.60—2.73 (m, 8 H, $(CH_2)_4$); 2.77, 2.79 (both s, 3 H each, Me); 2.95—3.38 (four q, 2 H, CH_2); 5.34—5.40 (two m, 1 H, CH); 7.41—7.82 (m, 5 H, Ph); for the minor diastereomer, δ: 2.99 (q, J_{gem} = 15.47 Hz,

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$^3J_{H,H}$ = 8.17 Hz); 3.35 (q, J_{gem} = 15.47 Hz, $^3J_{H,H}$ = 3.51 Hz); for the major diastereomer, δ: 3.13 (q, J_{gem} = 15.93 Hz, $^3J_{H,H}$ = 7.11 Hz); 3.23 (q, J_{gem} = 15.93 Hz, $^3J_{H,H}$ = 3.74 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.26, 21.28 (C(5)); 24.04, 24.19 (C(6)); 25.59, 28.20 (CH_3); 27.79, 28.05 (C(4)); 29.77, 29.80 (C(7)); 44.07, 46.03 (CH_2); 84.89, 85.05 (CH); 121.86, 123.11 (C(3a)); 128.17, 128.22 (C_o)*; 128.54, 128.62 (C_m); 133.26, 133.28 (C_p); 137.11 (C_{ipso}); 154.14, 154.63 (C(1a)); 197.19, 197.74 (C=O). ^{125}Te NMR ($CDCl_3$), δ: 1177.8, 1179.5.

Compounds **3b** and **3c** were obtained analogously.

1-Bromo-1-methyl-3-(4-nitrobenzoyl)methyl-1,3,4,5,6,7-hexahydro-2,1λ^4-benzoxatellurole (3b). The yield was 60%, light yellow needles, m.p. 147—148 °C (from chloroform—methanol (1 : 3)). Found (%): C, 38.42; H, 3.43. $C_{16}H_{18}BrNO_4Te$. Calculated (%): C, 38.75; H, 3.67. ^{1}H NMR ($CDCl_3$), δ: 1.60—2.76 (m, 8 H, $(CH_2)_4$); 2.76, 2.80 (both s, 3 H each, CH_3); 2.96—3.44 (four q, 2 H, CH_2); 5.28—5.76 (two m, 1 H, CH); 8.10 (d, 2 H, H-*o*,*o*´, *J* = 8.87 Hz); 8.32 (d, 2 H, H-*m*,*m*´, *J* = 8.87 Hz); for the minor diastereomer, δ: 3.02 (q, J_{gem} = 15.51 Hz, $^3J_{H,H}$ = 8.27 Hz); 3.40 (q, J_{gem} = 15.51 Hz, $^3J_{H,H}$ = 3.51 Hz); for the major diastereomer, δ: 3.15 (q, J_{gem} = 15.67 Hz, $^3J_{H,H}$ = 7.40 Hz); 3.27 (q, J_{gem} = 15.67 Hz, $^3J_{H,H}$ = 3.59 Hz).

1-Bromo-3-(4-methoxybenzoyl)methyl-1-methyl-1,3,4,5,6,7-hexahydro-2,1λ^4-benzoxatellurole (3c). The yield was 45%, colorless crystals, m.p. 161—163 °C (from chloroform—methanol (1 : 3)). Found (%): C, 42.43; H, 4.37. $C_{17}H_{21}BrO_3Te$. Calculated (%): C, 42.46; H, 4.41. ^{1}H NMR ($CDCl_3$), δ: 1.59—2.72 (m, 8 H, $(CH_2)_4$); 2.72, 2.76 (both s, 3 H each, Me); 2.88—3.29 (four q, 2 H, CH_2); 3.84 (s, 3 H, OMe); 5.27—5.74 (two m, 1 H, CH); 6.92 (d, 2 H, H-*m*,*m*´, *J* = 6.89 Hz); 7.92 (d, 2 H, H-*o*,*o*´, *J* = 6.89 Hz); for the major diastereomer, δ: 2.92 (q, J_{gem} = 15.32 Hz, $^3J_{H,H}$ = 8.13 Hz); 3.26 (q, J_{gem} = 15.32 Hz, $^3J_{H,H}$ = 3.63 Hz); for the minor diastereomer, δ: 3.06 (q, J_{gem} = 15.74 Hz, $^3J_{H,H}$ = 7.14 Hz); 3.16 (q, J_{gem} = 15.74 Hz, $^3J_{H,H}$ = 3.85 Hz).

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* The atomic positions are given with respect to the C=O group.