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Radical-Mediated Imidoylation of Telluroglycosides. Insertion of Isonitriles into the Glycosidic Carbon–Tellurium Bond

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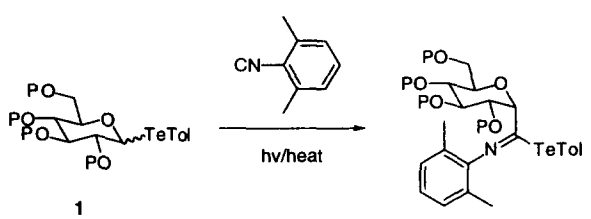
Abstract: Telluroglycosides react with isonitriles under photo-thermal conditions to give 1-telluroimidoylglycosides. The reaction proceeds by atom transfer radical reaction to form an imidic C-Te bond, which can be substituted to a C-C bond and C-O bond under oxidative conditions.

Recently, radical-mediated carbonylation or imidoylation reactions with carbon monoxide or isonitriles have attracted much attention as a valuable synthetic method for the synthesis of a variety of carbonyl and imidoyl compounds.[1, 2] We have already reported that glycos-1-yl radicals are generated from telluroglycosides, and that they react with alkynes in an atom transfer manner under photo-thermal conditions.[3] While the trapping of the glycos-1-yl radicals with carbon monoxide or isonitrile would provide a synthetic route to 1-acylglycosides which comprise important biologically active compounds,[4, 5] this possibility has not yet been tested.[6] Here we report that the radical generated from telluroglycoside **1** reacts with isonitriles in an atom transfer manner to give the corresponding 1-telluroimidoylglycoside **2** under photo-thermal conditions (Eq. 1).



(1)

1
a: P = Ac, **b**: P = Bz, **c**: P = Bn

2

We initially investigated the radical-mediated carbonylation of 1-telluroglycoside **1a** under various CO pressure (55-95 atm) at 50–120 °C in benzene with or without photo irradiation in an autoclave.[7] However, the desired acyl telluride could not be detected, and only the recovery of **1a** was observed. Since the C–Te bond of acyl tellurides is labile,[8] the result may be due to the instability of the product under the reaction conditions.

We next focused on isonitriles in the hope that a change in the property of the C-Te bond of the product would favor the formation of the product. The desired transformation was accomplished by combining the telluroglycoside **1a** and 2,6-dimethylphenylisonitrile (2.0 equiv.) in degassed C_6D_6 at 100 °C in a sealed NMR tube under UV lamp irradiation [Rayonet RMR-600 equipped with RMR-3500Å lamp (4.5 W x 8)], and the

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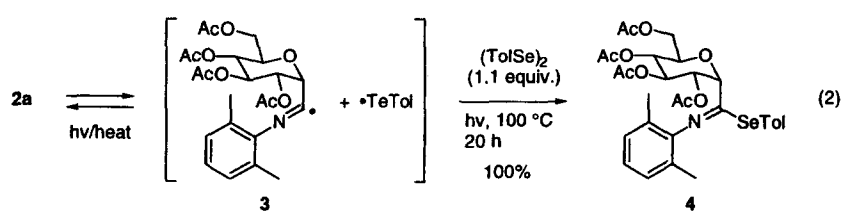
progress of the reaction was monitored by ^{1}H NMR. The NMR monitoring indicated steady increase of a single product, although the progress of the reaction was slow. After 10 h, the desired product **2a** was isolated in 65% yield together with 30% recovery of **1a** (Table 1, entry 1).[9] The reaction was very slow even at 140 ℃ without photo irradiation, but still afforded the desired adduct in 43% yield after 50 h. The NMR analysis of the product revealed that the α-anomer was formed selectively (>97% stereochemical purity), and the corresponding β-anomer was not detected within experimental error. The use of 1 equiv. of isonitrile slightly decreased the yield (44%). Addition of a radical initiator (0.1 equiv. of AIBN) as well as a radical chain inhibitor (0.1 equiv. of hydroquinone) had no effect on the reaction (44 % and 43 %, respectively, with 1 equiv. of the isonitrile). These results are consistent with the fact that a stoicheometric amount of the glycosyl radical is generated by a non-chain mechanism.[3] Alkyl substituted isonitriles (*n*-octyl- and *c*-hexylisonitrile) were less reactive, and they gave only 5–10% of the desired products under identical conditions.

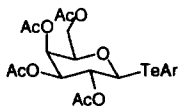
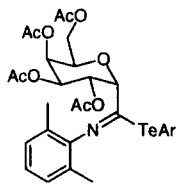
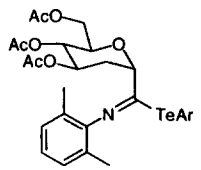
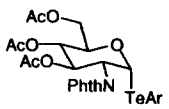
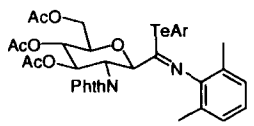
A variety of telluroglycosides was found to react with 2,6-dimethylphenylisonitrile at 100–120 ℃ with UV irradiation, and the results are summarized in Table 1. Since the product slowly decomposed under the reaction conditions (see below), the reaction was terminated before the starting telluroglycoside was completely consumed in all cases. Practically no decomposition of either the product or the starting materials was observed under the conditions described in Table 1. The recovered starting materials could be used for the reaction. The reaction was slightly sensitive to the property of the protective group, and the acyl-protected telluroglycosides showed higher reactivity than the alkyl-protected ones (entries 1–3). The reaction was insensitive to the stereochemistry of the C-4 hydroxyl group (entry 4), but the property of the C-2 substituent was found to have pronounced effects both on the reactivity and on the stereoselectivity. In the reaction of 1-tolyltelluro-2-deoxy-*D*-glycopyranoside derivative, the α-isomer of the desired product formed in 56% yield together with formation of 3,4,5-tri-O-acetyl-glycal in 13% yield (entry 5). The reaction of 2-phthaloyl protected 2-deoxy-2-amino-D-glycopyranoside derivative was slow, and resulted in an exclusive formation of the β-isomer (>95% selectivity).[10]

As in the case of acyl tellurides,[8] the C–Te bond of the products was found to be unstable, and homolytic cleavage of the C–Te bond of the product generated the corresponding imidoyl radical species under the reaction conditions.[11] Thus, thermolysis of **2a** in the presence of diaryl diselenide at 100 ℃ under UV irradiation for 20 h afforded the corresponding imidoyl selenide **4** in quantitative yield (eq. 2). Without diselenide, **2a** slowly decomposed, and 64% of **2a** was recovered after heating at 100 ℃ for 40 h. Under these conditions, neither telluroglycoside **1** nor the corresponding selenoglycoside was detected. These results



(2)

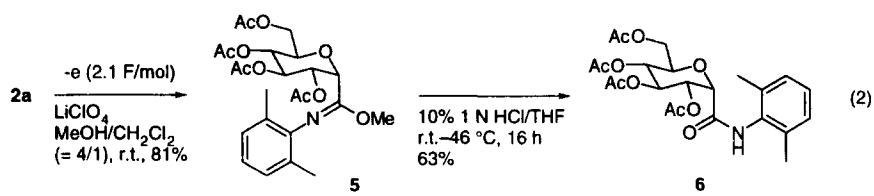
Table 1. Photochemical and Thermal Trapping of Isonitrile with Telluroglycosides.[a]

Entry	Telluroglycoside	Conditions	Product	%Yield[b]
1	**1a**	100 ℃, 10 h	**2a**	65 (92)[c]
		100 ℃, 5 h[d]		65 (96)[c]
		140 ℃, 50 h[e]		43
2	**1b**	100 ℃, 40 h	**2b**	76 (97)[c]
3	**1c**	100-120 ℃, 55 h	**2c**	38 (68)[c]
4		100 ℃, 40 h		80 (100)[c]
5		100 ℃, 40 h		56 (84)[f]
6		120 ℃, 50 h		29 (96)[c]

[a]The reaction was carried out by heating a solution of telluroglycoside and 2,6-dimethylphenylisonitrile (2.0 equiv.) in degassed C_6D_6 in a NMR tube under UV lamp irradiation (Rayonet RMR-3500Å, 4.5 W x 8). [b]Isolated yield. [c]Yield based on the converted telluroglycoside. [d]High-pressure Hg lamp (400W) was used as light source. [e] The reaction was carried out in the dark. [f]3,4,6-Tri-*O*-acetyl-*D*-glucal was formed in 13% yield.

indicated that homolytic C–Te bond cleavage of **2** took place smoothly to give the corresponding imidoyl radical **3**, while the subsequent C-C bond cleavage of **3** to form the glycos-1-yl radical was unfavorable.

The C-Te bond of the products was found to be useful for further synthetic transformations for the synthesis of 1-acylglycosides. For example, the C–Te bond of **2a** was substituted to a C–O bond to form the



(2)

corresponding imidic ester **5** in good yield by electrochemical oxidation in the presence of MeOH (0.1 M $LiClO_4$ solution of $MeOH/CH_2Cl_2$) at room temperature.[12] The imidic ester **5** was hydrolyzed to 1-carbamoylglycoside **6** by acid treatment (eq. 2).

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9. Spectra data of **2a**: IR (KBr) 1750 (s), 1625 (m), 1370 (m), 1230 (s), 1090 (m), 1030 (s); ^{1}H NMR (300 MHz, $CDCl_3$) 1.98 (s, 3 H), 2.01 (s, 3 H), 2.08 (s, 3 H), 2.10 (s, 3 H), 2.22 (s, 3 H), 2.27 (s, 3 H), 2.38 (s, 3 H), 4.11 (dd, J = 12.0, 2.4 Hz, 1 H), 4.24 (dd, J = 12.3, 5.3 Hz, 1 H), 4.79 (ddd, J = 10.2, 5.1, 2.2 Hz, 1 H), 4.87 (d, J = 6.9 Hz, 1 H), 5.01 (dd, J = 10.2, 9.2 Hz, 1 H), 5.11 (dd, J = 9.9, 6.6 Hz, 1 H), 6.19 (t, J = 9.5 Hz, 1 H), 7.01-7.11 (m, 5 H), 7.69 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 17.96, 18.29, 20.54, 20.63, 20.66, 21.33, 62.30, 68.83, 70.31, 70.70, 71.14, 74.07, 108.31, 124.82, 125.26, 126.40, 128.86, 128.97, 130.87, 139.90, 141.66, 142.24, 151.48, 161.53, 169.78, 169.87, 170.20, 170.87; FAB-MS (matrix: 3-nitrobenzylalcohol) m/z: 684 ($M + H^+$); Anal. Calcd for $C_{30}H_{35}NO_9Te$: C, 52.90; H, 5.18; N, 2.06. Found: C, 52.64; H, 5.14; N, 2.02.
10. The formation of the α-isomer can be explained by considering the anomeric effect of the glycos-1-yl radicals. However, the origin of the β-selectivity is not clear at the present time. One possible explanation may be an involvement of an intramolecualr participation of the polar C-2 phthaloyl group to the glycos-1-yl radical to shield the α-face, because such acyloxy group participation and rearrangement have already been reported. See, Giese, B.; Dupuis, J.; Gröninger, K.; Hasskerl, T.; Nix, M.; Weizel, T. *Substituent Effects in Radical Chemistry*; Viehe, H. G.; Janousek, Z.; Merényi, R., Eds; D Reidel Publishing Company: Dordecht, 1986; p283.
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