FIRST CONSTRUCTION OF BENZOTELLURAZEPINE RING SYSTEM, 4-METHOXY-1,5-BENZOTELLURAZEPINES[1]

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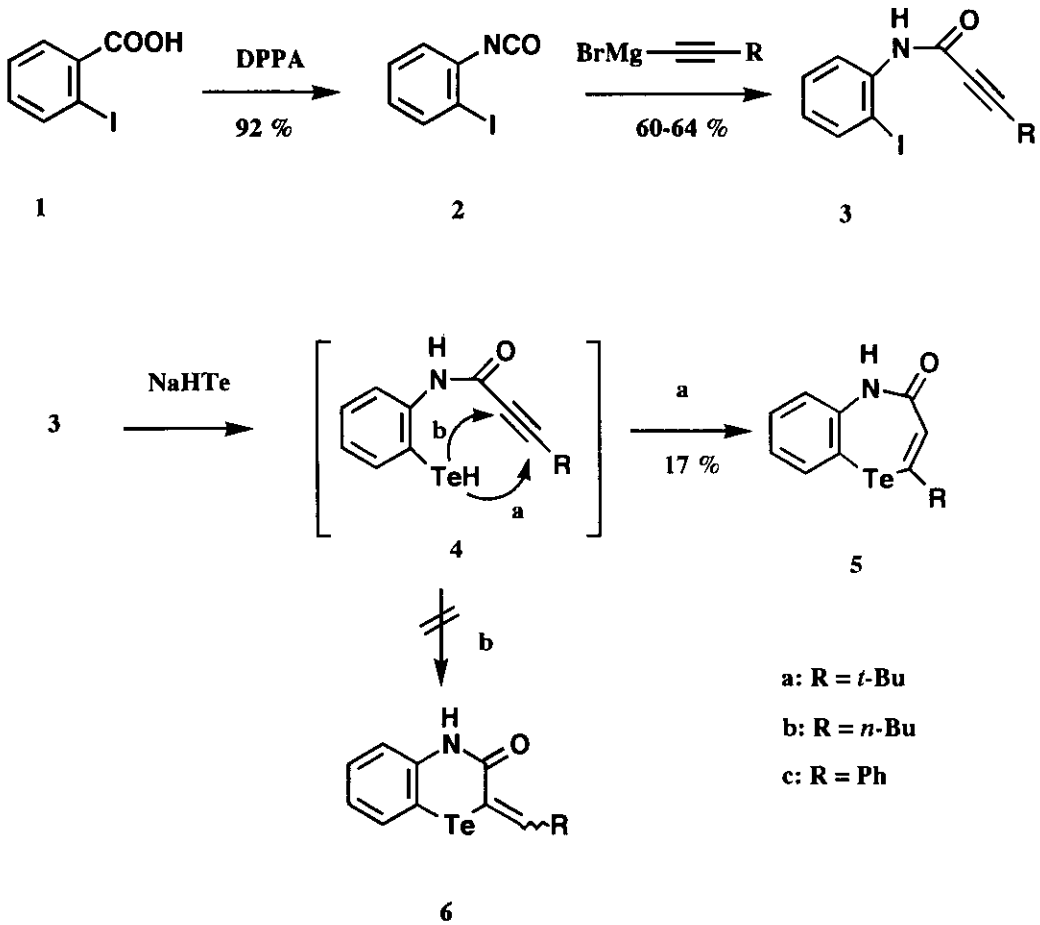
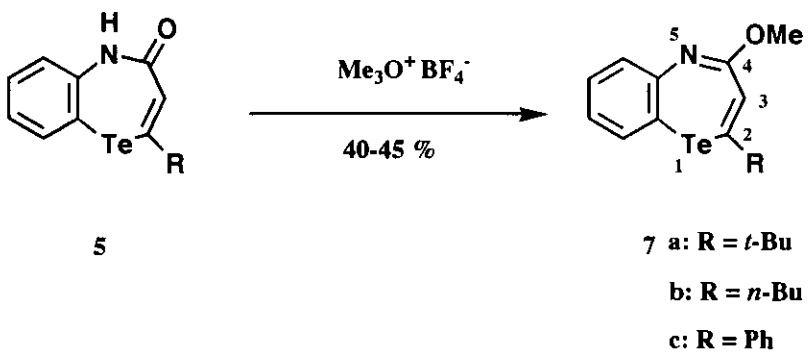
Abstract - *o*-Iodopropiolanilides (**3**) reacted with sodium hydrogen telluride to give 1,5-benzotellurazepinones (**5**) *via* intramolecular cyclization of the presumable phenyltellurole intermediates (**4**). The lactams (**5**) were converted into the title lactim compounds, 4-methoxy-1,5-benzotellurazepines (**7**) by treatment with trimethyloxonium tetrafluoroborate.

The chemistry of thiazepine systems, seven-membered heterocycles containing both atoms of sulfur and nitrogen has been reviewed.[2] Monocyclic 1,4-thiazepines [3,4] have been prepared by the ring-expansion of 4*H*-thiapyran-1,1-dioxides. The syntheses of their benzo derivatives, 1,4- and 1,5-benzotiazepine ring systems were described by Hofmann and Fischer[5] and by Kaupp *et al.*;[6] acid-catalyzed cyclization have been employed for the preparation of these compounds. Photocycloaddition reaction[7] of benzotiazole with acetylene compounds also gave 1,5-benzotiazepines. Among them, concerning with the synthesis of their telluro analogues, tellurazepine rings, only one paper have been reported until now. 1,4-Dibenzo[*b,f*]tellurazepine[8] has been prepared by the thermolysis of 9-azidoxanthene in 1987. Neither monocyclic tellurazepines nor benzotellurazepines have yet been known.

In recent years we have been investigating the syntheses of novel fully unsaturated seven-membered heterocycles[9] containing tellurium atom. More recently, a convenient synthetic route for the preparation of tellurochromones[10] has also been reported. Our synthetic strategy for the preparation of these compounds is based on cyclization of the tellurol



Scheme 1



Scheme 2

moiety to a triple bond. In this connections, we were interested in the synthesis of the title compounds. Here, we report the extension of increasing interest in our methodology for preparing the tellurium-containing heterocycles.

The first subgoal is the preparation of tellurazepinones (**5**). The synthesis of **5** from *o*-iodobenzoic acid (**1**) is shown in Scheme 1. *o*-Iodophenylisocyanate (**2**) was easily prepared from **1** *via* one step according to the diphenylphospholic azide (DPPA) procedure reported by Shioiri and Yamada.[11] *o*-Iodopropiolanilides (**3**) were successfully obtained with forming sp^2 -sp carbon bond by the reaction of the isocyanate (**2**) with the Grignard reagents. **2** reacted smoothly with equal amount of ethynylmagnesium bromides in THF at 0 °C to afford the anilides (**3**)[12] as a sole product in 60-64 % yields. We examined our original synthetic route[10] for the synthesis of the 1,5-benzotellurazepine skeleton. Treatment of **3** with sodium hydrogen telluride,[13] generated *in situ* from tellurium powder and sodium borohydride in DMF at 90-100 °C, resulted in a direct ring closure to give the desired 1,5-benzotellurepinones (**5**)[14] as a sole characterized product. No six-membered cyclization product (**6**) was obtained because of the proceeding of Michael-type addition in **4** *via* path a.[15] In order to introduce conjugated double bond, the lactams (**5**) were treated with trimethyloxonium tetrafluoroborate in dichloromethane at 0 °C to afford 4-methoxy-1,5-benzotellurazepines (**7**)[16] in 40-45 % yields.

The tellurazepinones (**5a-c**) are quite stable crystalline products, however, even the tellurazepines (**7a**), having a bulky substituents such as *tert*-butyl group at 2 position, are thermally instable probably owing to tellurium extrusion. Further studies on details of the stability and reactivities of these novel compounds (**5**,**7**) are in progress.

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12. All new compounds exhibited satisfactory elemental and spectroscopic data. Selected data for **3a** (R=*t*-Bu): 63 % yield, colorless leaflets, mp 65-67 °C. **3b** (R = *n*-Bu): 60 % yield, colorless leaflets, mp 77-80 °C. **3c** (R = Ph): 64 % yield, yellow prisms, mp 103-104 °C.
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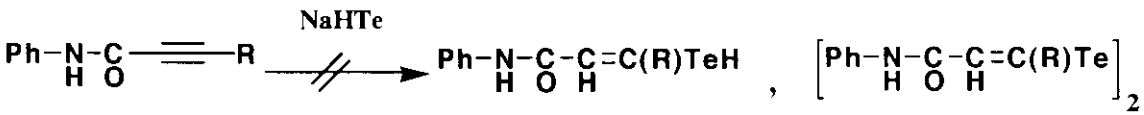
14. Selected data for **5a** (R=*t*-Bu): 17 % yield, pale yellow prisms (acetone - *n*-hexane), mp 150-151 °C. IR (cm^{-1},KBr): 3176 (NH), 1652 (C=O). ^{1}H-NMR (400 MHz): 1.18 (9H, s, *t*-Bu), 6.58 (1H, s, 3-H), Ph-H [7.05 (1H, dd, *J* = 7.3, 7.7 Hz), 7.16 (1H, d, *J* = 7.7 Hz), 7.36 (1H, dd, *J* = 7.3, 7.7 Hz), 7.87 (1H, d, *J* = 7.7 Hz)], 8.09 (1H, br, NH). ^{13}C-NMR (100 MHz): 29.45 (q), 40.63 (s), 113.69 (s), 123.06 (d), 128.01 (d), 129.19 (d), 130.10 (d), 139.34 (d), 141.38 (s), 151.74 (s), 170.59 (s). HRMS m/z: Calcd for $C_{13}H_{15}NOTe$: 331.0216. Found: 331.0227. *Anal.* Calcd for $C_{13}H_{15}NOTe$: C, 47.48; H, 4.60; N, 4.26. Found: C, 47.68; H, 4.64; N, 4.12. **5b** (R=*n*-Bu): 17 % yield, pale yellow prisms (acetone - *n*-hexane), mp 148-150 °C. **5c** (R=Ph): 17 % yield, pale yellow prisms (acetone - *n*-hexane), mp 184-186 °C.
15. An alternative mechanism for the formation of **5** would involve an addition of NaHTe to a triple bond at first. This possibility, however, was eliminated by the fact that treatment of propiolanilide (**8**) with NaHTe under the reaction condition used for the preparation of **5** did not gave the adduct (**9**) or the corresponding ditelluride (**10**).



8 **9** **10**

16. Selected data for **7a** (R=*t*-Bu): 45 % yield, pale yellow oil. ^{1}H-NMR (400 MHz): 1.16 (9H, s, *t*-Bu), 3.89 (3H, s, OMe), 6.40 (1H, s, 3-H), Ph-H [6.82-7.40 (3H, m), 7.75 (1H, dd, *J* =1.1, 7.5 Hz)]. HRMS m/z: Calcd for $C_{14}H_{17}NOTe$: 345.0373. Found: 345.0357. **5b** (R=*n*-Bu): 40 % yield, pale yellow oil. **5c** (R=Ph): 42 % yield, pale yellow oil.

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