Synthesis of Annelated 1,2,3-Selena- or -Thia-diazoles†

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D. Bhaskar Reddy,* A. Somasekhar Reddy and V. Padmavathi

Department of Chemistry, Sri Venkateswara University, Tirupati, 517 502, India

The reaction of semicarbazones of 3,5-diphenylcyclohex-2-enone **2** and 3,5-diphenylcyclohexanone **8** with selenium dioxide and thionyl chloride resulted in annelated 1,2,3-selena- and thia-diazoles **3**, **4**, **5**, **9** and **10**.

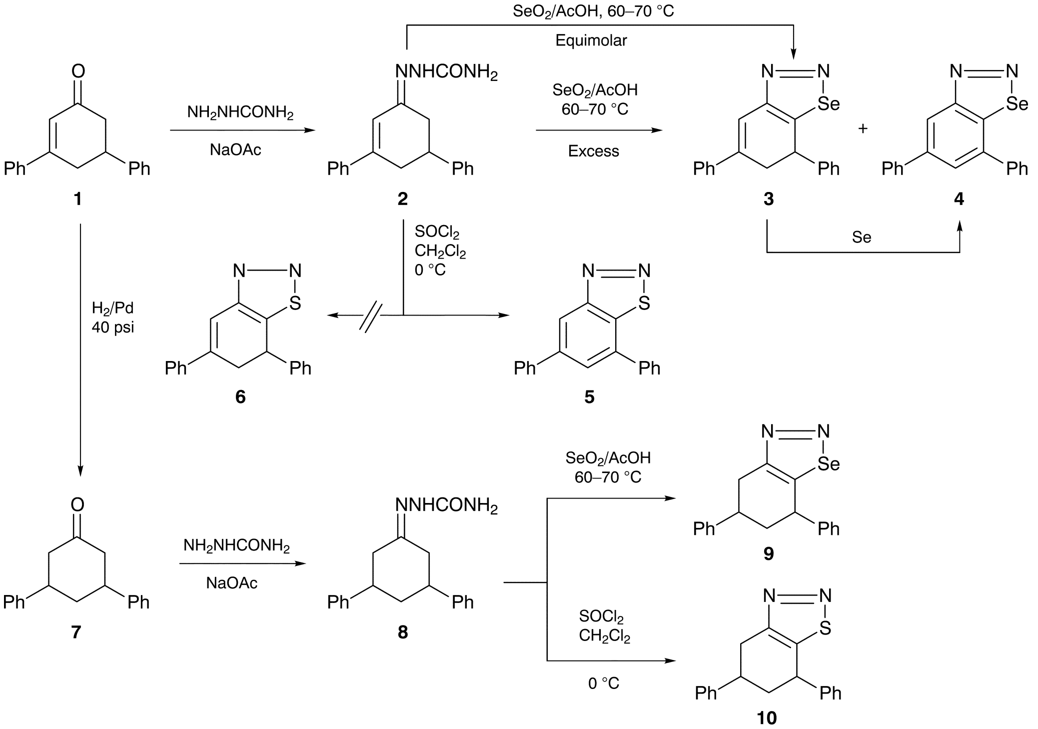
In recent years there has been a great deal of interest in annelated heterocycles for designing novel structures capable of performing a variety of functions. Some functionalized bicyclic annelated 1,2,3-selena- and thia-diazoles were found to be potential bioactive agents.[1,2] We recently reported the synthesis of 5,7-diaryldihydropyrido[3,4-*d*][1,2,3]selena or thiadiazoles[3] and 5,7-diaryl-6,6-dimethoxycarbonyldihydrobenzo[3,4-*d*][1,2,3]selena or thiadiazoles.[4] The α-keto methylene functionality in 2,6-diaryl-4-piperidones and 2,6-diaryl-4-oxocyclohexane-1,1-dicarboxylates was responsible for formation of the annelated bicyclic systems. In a continuation of our study, we examined the reaction of cyclic ketones and cyclic enones to obtain their fused 1,2,3-selena- or -thiadiazoles, hitherto unreported in the literature.

The reaction of the semicarbazone of 3,5-diphenylcyclohex-2-enone **2** when performed with selenium dioxide in acetic acid in equimolar proportions at 70 °C gave 5,7-diphenyl-6,7-dihydrobenzo[3,4-*d*][1,2,3]selenadiazole **3** (62%, 85 °C) (Scheme 1). The ^{1}H NMR spectrum of **3** showed δ_H 4.62 (t, 7-H), 3.24 (d, 6-H) and 5.30 (s, 4-H).

On the other hand, when **2** was subjected to the Hurd–Mori reaction process[5] with excess thionyl chloride at −10 °C for 3 h and when treated with dichloromethane and saturated sodium carbonate solution, a fully aromatized product, 5,7-diphenylbenzo[3,4-*d*][1,2,3]thiadiazole **5** (65%, 96 °C) was obtained in a one-pot reaction. The formation of this product is contrary to the expected dihydrothiadiazole **6**. The signal at δ_H 7.22–7.85 in its ^{1}H NMR spectrum confirms the formation of **5** only.

These results are rather surprising as the analogous reaction of 4-piperidones[3] and 4-oxocyclohexanedicarboxylates[4] gave exclusively the respective tetrahydro-1,2,3-thiadiazoles. The observed aromatization might be attributed to the presence of a double bond in conjugation with the phenyl moiety. The probable mechanism for this can be explained as follows (see mechanism in Scheme 2). The intermediate *N*-amidodihydrothiadiazole *S*-oxide **11** undergoes Pummerer like rearrangement with thionyl chloride to *N*-amidothiadiazolium chloride[6] **13**. The expected dihydrothiadiazole **6** should have been formed by the loss of CO_2 and NH_3. However, another mole of $SOCl_2$ was consumed leading to the corresponding imidoyl chloride **14**. Elimination of HCl is favoured at this stage and a cyclic diene **15** is formed which is highly unstable. Subsequent aromatization of the latter led to **5**.

Based on the results with thionyl chloride the reaction of **2** with excess selenium dioxide (1:2 ratio) was again carried out under similar conditions. A mixture of products were obtained in 3:2 proportion. The two were separated through a column of silica gel. The major product was found to have a melting point of 85 °C, similar to that of **3**. A mixed melting point of the major product and **3** was unchanged, indicating the identity of this product and **3**. Furthermore, the NMR spectrum of this sample was also



Scheme 1

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*To receive any correspondence.

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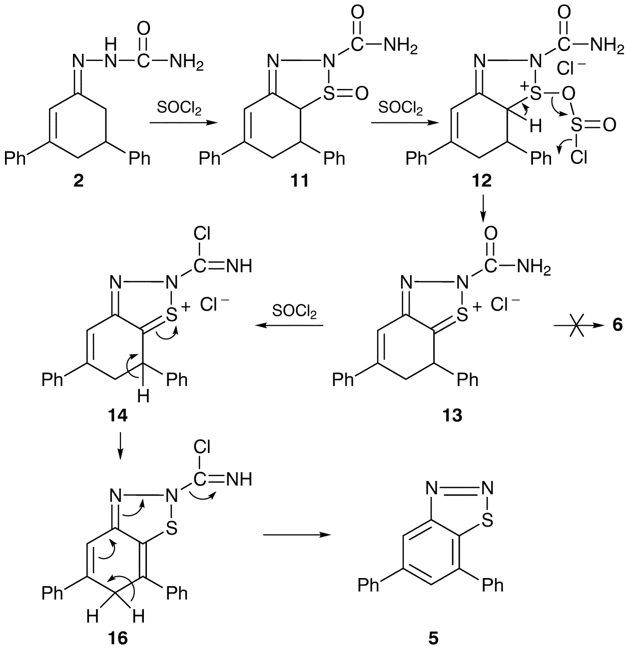

Scheme 2

the same as that of **3**. On the other hand, the minor product whose melting point is 125 °C exhibited a multiplet at δ_H 7.25–7.94 in its NMR spectrum similar to that of **5** indicating that it is the fully aromatized **4**. Obviously, the formation of **4** might be due to the deposited selenium.[7,8] This has been substantiated by the fact that when **3** was further made to react with selenium powder in an equimolar ratio in an inert atmosphere, aromatized product **4** was obtained. This confirmed that dehydrogenation is effected due to the excess of selenium (Scheme 1).

Later, in order to ascertain the influence of the double bond, the cyclic enone was subjected to catalytic hydrogenation with H_2/Pd under pressure (40 psi) at room temperature for 1 h. The resultant 3,5-diphenylcyclohexanone **7** was annelated to give the 1,2,3-selena- and thia-diazoles with selenium dioxide (both equimolar and excess) and thionyl chloride (excess) respectively, *via* its semicarbazone **8**. The ^{1}H NMR spectra of the products formed proved that they are 5,7-diphenyltetrahydrobenzo[3,4-*d*][1,2,3]-selenadiazole (68%, 112 °C) **9** and -thiadiazole (65%, 93 °C), **10**. The δ_H values of **9** and **10** at around 3.52–3.61 (t), 3.01–3.12 (m), 2.81–2.90 (m) and 2.10–2.21 (m) were due to protons at C-7, C-5, C-4 and C-6, respectively. This clearly shows that the presence of a double bond in **1** appears to be mainly responsible for the formation of aromatized products (**4** and **5**) during their cyclocondensation pathway.

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