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Novel Heterocycles: 1,3,4-Oxadithiolane, 1,3,4-Oxadiselenolane, 1,3-Oxathietane and 1,3-Oxaselenetane Derivatives

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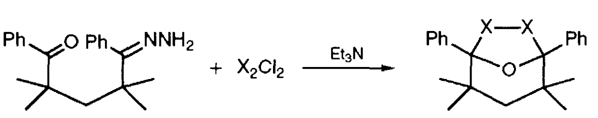
The reaction of the monohydrazone **1** of 2,2,4,4-tetramethyl-1,5-diphenylpentane-1,5-dione with S_2Cl_2 affords a bicyclic 1,3,4-oxadithiolane derivative **2**, which gives an equilibrium mixture of a 1,3-oxathietane **7** and its ring-opened isomer **6** on treatment with $P(NMe_2)_3$, whilst the 1,3,4-oxadiselenolane **3** prepared from **1** and Se_2Cl_2 affords a 1,3-oxaselenetane **8** and a cyclic ketone **9** on treatment with the same reagent.

Recently we reported that thionation of nonenolizable 1,ω-diketones gives bicyclic 1,3-dithietanes (thiocarbonyl dimer) and 1,3,4-trithiolanes (trithioozonide) as principal products, although the dithione becomes the major product in the case of ω = 7.[1] In this connection we have examined the reaction of the monohydrazone **1** of 2,2,4,4-tetramethyl-1,5-diphenylpentane-1,5-dione with S_2Cl_2[2] and Se_2Cl_2[3] with expectation of obtaining novel heterocycles which possess oxygen–sulfur[4] and oxygen-selenium mixed ring systems.

The hydrazone **1** was prepared in 59% yield by treatment of the corresponding ketone with hydrazine hydrate in hexane–methanol. A solution of S_2Cl_2 (2 equiv.) in benzene was added to a solution of **1** and triethylamine in benzene and then the mixture was refluxed for 5 h. Chromatographic purification (silica gel) gave a bicyclic 1,3,4-oxadithiolane derivative **2** (56%).† The use of 1 equiv. of S_2Cl_2 gave **2** in decreased yield (25%). Similarly the reaction of **1** with Se_2Cl_2 (2 equiv.) in the presence of triethylamine in refluxing toluene gave a 1,3,4-oxadiselenolane derivative **3** (21%). The oxadithiolane **2** and oxadiselenolane **3** thus obtained provide hitherto unknown ozonide analogues in which two oxygen atoms are replaced with two sulfur and two selenium atoms,[2,5] although the formation of a 2,5-dimethylene-1,3,4-oxadithiolane derivative was previously suggested.[6]

Compounds **2** and **3** correspond to intramolecular cyclisation products of thiosulfine **4** and selenoselenine **5**.[3,7] However, their trapping by 1,3-dipolar cycloaddition with dimethyl acetylenedicarboxylate was unsuccessful. The thione **6** may exist as an intermediate in the formation of **2** because it was isolated in a small amount when the reaction of **1** with S_2Cl_2 was quenched at the early stage and it reacts with S_2Cl_2 to give **3**.

The desulfurization of **2** and deselenation of **3** were examined. Treatment of **2** with $P(NMe_2)_3$ (2 equiv.) in refluxing toluene for 5 h gave the thione **6** and 1,3-oxathietane **7**, which could not be isolated in pure form because interestingly they are in equilibrium with each other in solution. To our knowledge, this is the first observation of [2 +



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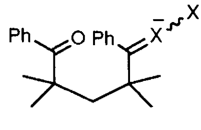
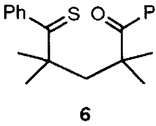
X = S, Se

2 X = S
3 X = Se



4 X = S
5 X = Se



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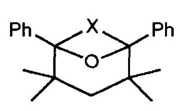
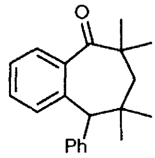


7 X = S
8 X = Se



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† All new compounds gave satisfactory analytical and spectral data. *Selected data*: **2**: yellow crystals, m.p. 226–227 °C; ^1H NMR δ ($CDCl_3$) 1.01 (s, 6H), 1.26 (s, 6H), 1.31 (d, *J* 14.2 Hz, 1H), 2.38 (d, *J* 14.2 Hz, 1H), 7.27–7.37 (m, 6H) and 7.54–7.56 (m, 4H); ^{13}C NMR δ ($CDCl_3$) 26.7 (q), 29.3 (q), 42.0 (s), 48.7 (t), 111.8 (s), 126.3 (d), 127.5 (d), 127.7 (d) and 140.0 (s); MS *m/z* 356 (M^+); UV (MeCN) λ_{max}/nm 372 (ε 129) and 308 (165). **3**: red–brown crystals, m.p. 237–238 °C; MS *m/z* 372 (M^+): UV (MeCN) λ_{max}/nm 444 (ε 151) and 350 (143). **6**: ^1H NMR δ ($CDCl_3$) 1.34 (s, 6H), 1.36 (s, 6H), 2.84 (s, 2H), 7.26–7.47 (m, 8H) and 7.64–7.66 (m, 2H); ^{13}C NMR δ ($CDCl_3$) 28.7 (q), 31.2 (q), 48.4 (s), 51.7 (t), 55.4 (s), 125.5 (d), 127.4 (d), 128.08 (d), 128.12 (d), 128.5 (d), 130.9 (d), 138.9 (s), 151.0 (s), 209.2 (s) and 265.5 (s); MS *m/z* 324 (M^+); UV (MeCN) λ_{max}/nm 569. **7**: ^1H NMR δ ($CDCl_3$) 0.99 (s, 6H), 1.19 (s, 6H), 1.75 (d, *J* 13.9 Hz, 1H), 2.59 (d, *J* 13.9 Hz, 1H) and 7.16–7.30 (m, 10H); ^{13}C NMR δ ($CDCl_3$) 22.7 (q), 26.7 (q), 40.9 (s), 53.0 (t), 98.8 (s), 124.9 (d), 127.19 (d), 127.23 (d) and 141.0 (s); MS *m/z* 324 (M^+). **8**: pale yellow crystals, m.p. 161–162 °C; MS *m/z* 372 (M^+). **9** (mechanism of formation of this compound is not clear): colourless crystals, m.p. 86–87 °C; ^1H NMR δ ($CDCl_3$) 0.94 (s, 3H), 1.10 (s, 3H), 1.40 (s, 3H), 1.42 (d, *J* 15.4 Hz, 1H), 1.48 (s, 3H), 2.22 (d, *J* 14.1 Hz, 1H), 4.68 (s, 1H), 6.87 (dd, *J* 7.6, 0.9 Hz, 1H), 7.00 (td, *J* 7.4, 1.2 Hz, 1H), 7.22 (td, *J* 7.6, 1.2 Hz, 1H), 7.43 (dd, *J* 8.0, 0.8 Hz, 1H), 7.50 (t, *J* 7.5 Hz, 2H), 7.59 (t, *J* 7.3 Hz, 1H) and 8.07 (d, *J* 7.3 Hz, 2H); ^{13}C NMR δ ($CDCl_3$) 29.2 (q), 29.8 (q), 33.6 (s), 33.7 (q), 33.9 (s), 34.9 (q), 47.7 (t), 56.3 (d), 125.3 (d), 127.2 (d), 127.6 (d), 128.6 (d), 128.7 (d), 129.1 (d), 132.9 (d), 134.1 (s), 139.8 (s), 145.7 (s) and 202.0 (s); MS *m/z* 292 (M^+).

2] cycloaddition of thiocarbonyl and carbonyl in a head-to-tail manner.[1] On the other hand, treatment of **3** (0.26 mmol) with $P(NMe_2)_3$ (0.55 mmol) in refluxing toluene for 5 h gave the 1,3-oxaselenetane **8** (17%), the benzosuberone **9** (17%), and $Se{=}P(NMe_2)_3$ (0.38 mmol) with recovery of **3** (13%). In contrast to **7**, the oxaselenetane **8** does not undergo thermal ring opening at ambient temperature. Successful syntheses of the 1,3-oxathietane and 1,3-oxaselenetane ring systems with a divalent sulfur and selenium have not been reported[8,9] and thus the present study may serve to open a new chemistry of these rather simple, but unexplored, heterocycles.

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