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THE LAWESSON REAGENT AS SELECTIVE REDUCING AGENT FOR SULFOXIDES[1]

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Abstract: Different functionalized sulfoxides can be selectively deoxygenated by Lawesson reagent to yield the corresponding sulfides in high amounts.

There is a great number of agents for the reduction of sulfoxides described in the literature. Among them phosphorus/sulfur containing compounds like P_2S_{10},[2] thiophosphinic, thiophosphonic and thiophosphoric acids,[3] dialkyldithiophosphoric acids[4] and thiophosphoryl bromide[5] are found.

Lawesson reagent (L.R.), well known as a thionating agent for "carbonyl compounds", has such reducing activity too. Lawesson and co-workers[6] described in one of their studies on organophosphorus compounds the formation of the corresponding sulfides and disulfides from DMSO and tetrahydrothiophene sulfoxide, respectively. In this paper we investigated the selective reactivity of L.R. against several functionalized sulfoxides.

The compounds **1**, **3**, **5**, **7**, **9** and **11**[7] were treated with L.R. in THF at room temperature. Quantitative transformation to the corresponding sulfides occurs only using one or more than one molecular equivalent of L.R..[8] Interestingly, no thionation of the ester function was observed also by using an excess of L.R. and refluxing the reaction mixture in THF, toluene and xylene, respectively. This fact has to be mentioned, because these conditions normally lead to corresponding thio analogs.[9]

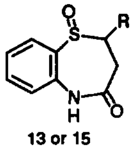
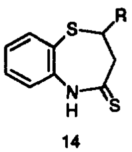
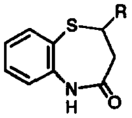
1 $R^1 = R^2 = Ph$	**2** $R^1 = R^2 = Ph$
3 $R^1 = R^2 = Bz$	**4** $R^1 = R^2 = Bz$
5 $R^1 = Ph; R^2 = Me$	**6** $R^1 = Ph; R^2 = Me$
7 $R^1 = Ph; R^2 = CH_2CH$	**8** $R^1 = Ph; R^2 = CH_2CH$
9 $R^1 = CH_3SCH_2; R^2 = Me$	**10** $R^1 = CH_3SCH_2; R^2 = Me$
11 $R^1 = Ph; R^2 = CH_2CO_2Me$	**12** $R^1 = Ph; R^2 = CH_2CO_2Me$

In contrast to these results lactams **13**[10] and **15**[11] undergo reduction of the sulfoxide function **and** thionation of the lactam group at room temperature as well as at -5° C.

As demonstrated in Table 1 (entry 1,2) no quantitative conversion to the thiolactams **14**[12] and **16**[13] takes place at the given molar ratios. Additionally entry 2 shows an interesting fact: besides compound **16** the reduced, not thionated lactam **18** was built too.

Variation of the conditions led to a selective progress of the reaction. An excess of L.R. (2.5 mol) and room temperature or -5° C yielded the thiolactams **14** and **16** quantitatively (entry 3,4). In contrast, a molar ratio 1:1 and a reaction temperature of -20°C exclusively led to the reduction of the sulfoxide function (entry 5,6). Lactams **17**[14] and **18**[15] were obtained without byproducts.[16]

Table 1. L.R.-Promoted Reduction of Lactam Sulfoxides

Entry	Substrates	Molar ratio Substrate : L.R.	Temp.	Solvent	Isolated compounds
1,2	 13 or 15	1 : 0.5 - 1	r.t. or -5° C	THF or CH_2Cl_2	 14 + 13 or 16 + 18 + 15
3,4	13 or 15	1 : 2.5	r.t. or -5° C	THF or CH_2Cl_2	14 or 16
5,6	13 or 15	1 : 1	-20° C	CH_2Cl_2	 17 or 18

13, 14, 17: R = H **15, 16, 18**: R = Ph

These results prove L.R. as a highly selective reagent for the reduction of functionalized sulfoxides.

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References and Notes

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7. Sulfoxides as well as sulfides are commercially available.
8. The reactions were monitored by TLC and GC; they were finished within 5 to 60 minutes.
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16. To avoid thionation, the remained L.R. has to be destroyed with ice-cooled 2N hydrochloric acid before warming up.

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