Formation of a Novel N–N Bond through SO Extrusion. Regioselective Synthesis of 1,2,6-Thiadiazine *S*-Oxides and Pyrazoles

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Summary The preparation of the 1,2,6-thiadiazine *S*-oxides (**3**) and their conversion into the pyrazoles (**4**) is described; the formation of (**4**) results from N–N bond formation following the extrusion of SO.

WE have already reported[1] on the versatility of (**1**) in the synthesis of heterocyclic compounds with one or two nitrogen atoms in the ring. We now report a new method for the synthesis of 1,2,6-thiadiazine *S*-oxides by reaction of (**1**) with thionyl chloride in pyridine or benzene–triethylamine as a solvent at room temperature. The results are summarized in the Table.

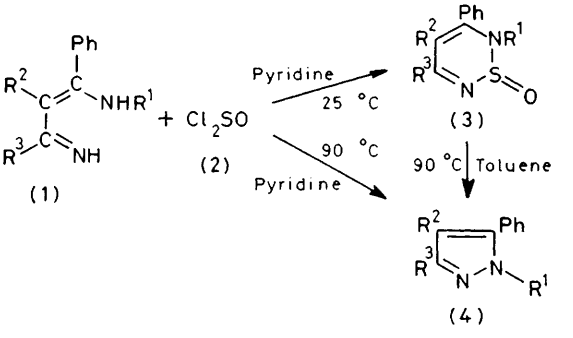

TABLE. Thiadiazine *S*-oxides (**3**) and pyrazoles (**4**) obtained from di-imines (**1**)

			(**3**)		(**4**)	
R^1	R^2	R^3	% Yield	M.p. (*t*/°C)	% Yield	M.p. (*t*/°C)
Ph	H	Ph	86	153 –154	93	138—139
p-MeC_6H_4	H	*p*-MeC_6H_4	87	184—185	90	173—175
p-MeC_6H_4	H	c-C_6H_{11} [a]	84	122—124	94	163—165
Ph	Me	Ph	80	133—135	86	122—124
p-MeC_6H_4	Me	*p*-MeC_6H_4	79	161—162	86	144—146
Ph	Me	*p*-MeC_6H_4	82	148—149	88	168—170
c-C_6H_{11}	Me	Ph	85	146—147	85	96—98
c-C_6H_{11}	Me	*p*-MeC_6H_4	84	160—161	84	147—149

[a] Cyclohexyl.

The hydrolysis of (**3**) with 6N-KOH at 60 °C yields the starting material (**1**). However, when (**3**) is heated in toluene at 90 °C the pyrazoles (**4**) are obtained in high yields (see Table), *via* N–N bond formation following the extrusion of SO. The compounds (**4**) can also be obtained *in situ* when (**1**) reacts with (**2**) in pyridine at 90 °C.[2]

A typical procedure for the synthesis of compounds (**3**) is as follows. Thionyl chloride (0·012 mol) was added to (**1**) (0·01 mol) in pyridine (50 ml) at 0 °C. The stirred mixture was warmed to room temperature; after 2 h 4N H_2SO_4 was added and compounds (**3**) were extracted into ether and purified by recrystallization from hexane. The pyrazoles (**4**) were obtained by heating (**3**) in toluene at 90 °C for 8 h, and were recrystallized from hexane following elimination of toluene *in vacuo*.

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[1] J. Barluenga, M. Tomás, V. Rubio, and V. Gotor, *J.C.S. Chem. Comm.*, 1979, 675, and references therein.
[2] The structures of (**4**; R^3 = Ph) were corroborated by an alternative synthesis by the reaction of 1,3-dicarbonyl compounds with phenylhydrazine. See J. Elguero and R. Jacquier, *Bull. Soc. chim. France*, 1966, 2832.