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Sulfidation of Alicyclic and Heterocyclic 1,3-Dicarbonyl Systems

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SULFIDATION OF ALICYCLIC AND HETEROCYCLIC 1,3-DICARBONYL SYSTEMS

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<u>Abstract</u> The synthesis of sulfides starting with anions of 1,3-dicarbonyl systems and disulfides is presented.

Anions of alicyclic and heterocyclic five- or six-membered 1,3-dicarbonyl compounds react with aromatic disulfides and other -S-S- systems, such as thiuramdisulfides, in DMF in the presence of potassium carbonate to yield sulfides. The heterocyclic systems studied include pyrazol-1,3-diones, barbituric acids, 6-hydroxy-pyrimidin-4-ones, 5-hydroxy-3(2*H*)-pyridazinones, 4-hydroxy-2-pyridones; and their benzo derivatives (e.g. coumarins and quinolones).

OH

OH

OH

OH

OH

OH

$$R^2$$
 R^1
 R^2
 R^2

Oxidation of the sulfides with peracids yields sulfones, while careful oxidation with H_2O_2 in alkaline medium affords the sulfoxides. The latter class of compounds are heteroanalogs of the well known cyclic tricarbonyl methane derivatives [SO instead of CO] which show a broad range of biological activity, especially in agricultural chemistry.

$$\begin{array}{c}
OH \\
Y \\
O \\
O
\end{array}
+
\left\{\begin{array}{c}
S \\
R \\
O \\
O
\end{array}\right\}_{2}$$

$$OH \\
S \\
S \\
C \\
O$$

$$OH \\
S \\
O \\
C$$

$$OH \\
S \\
O \\
O$$

R=
$$CH_3$$
, C_2H_5
R-R= $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$

Aliphatic thioethers of this type can not be prepared by the procedure described before. However, they are available by the reaction of the α -halogeno β -dicarbonyl systems or their corresponding iodonium ylids.¹⁻³

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