Tetrahedron Letters,Vol.27,No.33,pp 3911-3912,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

THIOCARBONYL TO CARBONYL GROUP TRANSFORMATION USING CuCl AND NaOH

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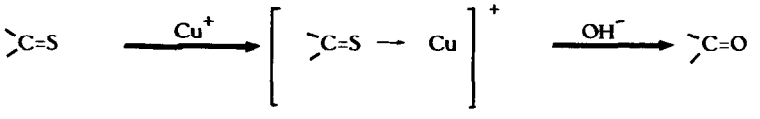
Abstract : A simple and efficient procedure for the rapid and mild conversion of thiocarbonyls to carbonyls is described.

Several methods are available for the title conversion. These oxidations involve the use of single oxygen[1], peroxo compounds[2] or oxides of selenium[3]. A catalytic cycle using telluroxide has also been developed[4,5]. However many of the recent methods use mild reagents that work because of the attraction of the soft cation NO^+ towards sulfur[6,7]. Even clay supported nitrates seem to work on this principle[8].

We wish to report a method that utilises the attraction of the soft Cu^+ towards sulfur to form a complex which undergoes a very rapid reaction with OH^- to give the corresponding oxo compound.



Hydrolysis of thioketones to ketones has been observed in boiling water[9]. Mono-thio-β-diketones are stable in basic medium[10], but basic hydrolysis of fluorinated mono-thio-β-diketones has been observed to proceed with C-C bond cleavage[11]. The major advantage of this method is the specificity and the rapidity with which it brings about this conversion without having to use carcinogenic reagents. It works well with a variety of thio compounds and a representative list of the compounds used to test the above reaction is given in the Table along with the yields and the melting points of the corresponding oxo compounds thus obtained.

In a typical reaction the thione (5 mmol) was added under N_2 atmosphere to a solution of CuCl (5 mmol) in 50 ml of dry degassed acetonitrile. A solid complex of the thione and the CuCl precipitated out. To this suspension was added 5 mmol of NaOH as a 10% aqueous solution. A dark colored solid precipitated out. After stirring for the required time the slurry was extracted with ether (3x30 ml) and the ether layers combined, dried and concentrated to give the ketone. Reactions run under identical conditions in the absence of CuCl led to isolation of the starting materials in greater than 95% yield.

Among the various thiones used to test this reaction Michler's thione was unusual in that it required six hours of refluxing in acetonitrile to effect 85% conversion. The reason for this is unknown.

TABLE

Substrate	Time in minutes	Temperature °C	Yield[a] %	m.p.[b] °C
Diphenylthiourea	20	25	100	240-1
Thiobenzamide	10	25	90	127
Thionicotinamide	10	25	88	129-30
1-Methyl-2-thiopyridone	20	25	96	31-2
Thiocoumarin	15	25	100	68-9
4,4'-Dimethylthiobenzophenone	10	25	100	95
Thioxanthione	15	25	100	207-9
Xanthione	15	25	100	174-5
Michler's thione	720	80	85	174-6
Thiocamphor	30	25	85	179-80

[a] No efforts were made to optimise the yields.

[b] The purity of the products was confirmed by comparison of the spectral data with those of authentic samples.

Acknowledgement : The authors wish to thank Professor V. Ramamurthy for a gift of thiones and helpful discussions.

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(Received in UK 18 June 1986)