

SYNLETT Spotlight 263

Carbon Disulfide (CS₂)

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Francisco Javier Iglesias-Sigüenza was born in Seville in 1981. He received his degree in chemistry at the University of Seville in 2004. Then, he joined Dr. R. Fernández's research group, where he is conducting his PhD research in the area of asymmetric synthesis and catalysis. His present research interests involve the synthesis and applications of new chiral N-heterocyclic carbenes prepared from hydrazines in asymmetric catalysis.

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Introduction

Carbon disulfide is a volatile liquid, colourless, inexpensive and commercially available reagent that has found a lot of applications in organic chemistry. It has been used to prepare organic building blocks, especially for the synthesis of various sulfur-containing derivatives such as sulfur heterocycles, dithiocarbonates, thioureas, thio-carbamates.

The problems associated with this reagent are that it is highly flammable and has one of the lowest autoignition temperatures; because of that it is necessary to take certain precautions with its use.

Compared to CO₂, CS₂ is more reactive toward nucleophiles and more easily reduced. These differences in reactivity can be attributed to the weaker π -donor ability of the sulfide centers, which makes the carbon more electrophilic. Therefore, it is widely used in the synthesis of organosulfur compounds, which can be used in industrial chemistry.

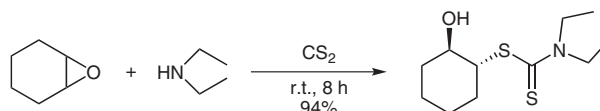


Figure 1

Abstract

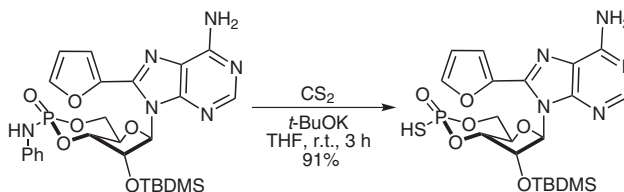
(A) One-pot Synthesis of Dithiocarbamates:

It is possible to prepare β -hydroxy dithiocarbamates with exclusive *trans*-stereochemistry from amines, epoxides and carbon disulfide in a one-pot procedure without the use of a catalyst or solvent. This reaction offers advantages such as low cost, high yields, reduced environmental impact and simple work-up. Furthermore, this reaction presents another advantage, since with unsymmetrical epoxides it is completely regioselective. Generally, secondary amines give higher yields than primary ones.¹



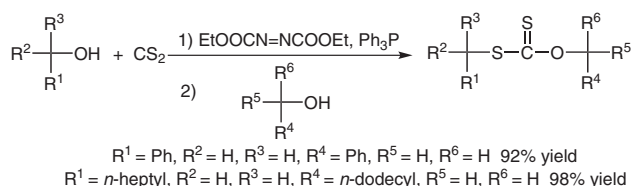
(B) Conversion of Phosphoramidates into Phosphorothioic Acids:

The stereospecific PN \rightarrow PX (X = O, S) conversion, that is to say, the transformation of P-chiral phosphoramidates, by replacement of an amidate function by oxygen or sulfur, in P-chiral derivatives of phosphorus acids is known as the Stec reaction.² Hereby, chiral phosphorothioic acids can be prepared from dialkyl phosphoramidate anions by means of carbon disulfide in a stereospecific way and with excellent yields.³

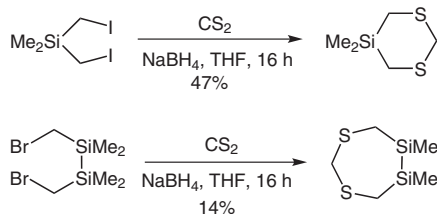


(C) *One-pot Synthesis of O,S-dialkyl Dithiocarbonates from Alcohols:*

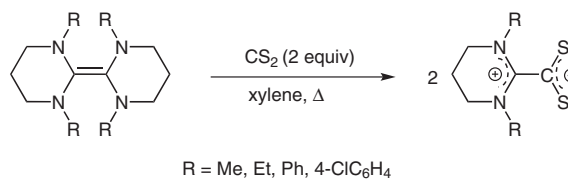
Carbon disulfide has been used in the preparation of *O,S*-dialkyl dithiocarbonates from a variety of primary, secondary and tertiary alcohols employing a novel Mitsunobu reaction. This is an efficient methodology to obtain these compounds with excellent yields under mild conditions.⁴

(D) *Synthesis of 1,3,5-Dithiasilinanones and 1,3,5,6-Dithiadisilapanes:*

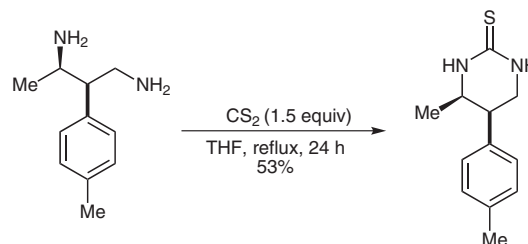
Carbon disulfide can be used as the source of $\text{CH}_2(\text{S}^-)_2$ to prepare dithiasilinanones and dithiadisilapanes from the corresponding dihalides. In a similar way, other mixed group 14/16 six- and eight-membered ring compounds were synthesized from the suitable halides.⁵

(E) *Synthesis of Imidazolium Carbodithioates (Used as Carbene Precursors):*

The CS_2 dipole existing in imidazolium carbodithioates can act as a carbene precursor. These carbodithioates can be synthesized from tetraaminoethylene derivatives. The corresponding carbene, obtained by warming the dimer, subsequently reacts as a nucleophile with carbon disulfide. If the amino substituent R is aliphatic, only a short and fast warming is needed; for R = aromatic, the zwitterion is only obtained after warming to reflux in xylene.⁶

(F) *Synthesis of Thioureas from 1,3-Diamines:*

In recent years, chiral thioureas have attracted attention due to their anti-HIV activities, among other reasons. It is possible to prepare chiral cyclic thioureas from enantiopure 1,3-diamines, without loss of enantioselectivity, using carbon disulfide.⁷



References

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