3-Mercaptopropionic Acid (3-MPA)

Compiled by Fabian Fischer

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Introduction

3-Mercaptopropionic acid (3-MPA) belongs to the family of mercaptans. 3-MPA is known for a long time and was already synthesized by Lovén in 1884. All major chemical suppliers sell the compound for a reasonable price nowadays. A convenient preparation is possible by the procedure of Gresham et al., who employed MPA for various organic syntheses. This interesting bifunctional compound is also known as a versatile chain transfer reagent in the telomerization of short oligomers for biotechnological applications.

Preparation

β-Propiolactone and sodium thiosulfate react easily to a stable thiosulfate intermediate. By the following acidification the desired product, mercaptopropionic acid (3-MPA) and sulfuric acid, are isolated in good yields.

Abstracts

3-MPA serves as a sulfur-transfer reagent in this reaction. With the procedure a wide range of aryl bromides are transformed into bis aryl sulfides in fair to good yields.

The transformation of fluorene to fluorenesbisphenoxy derivatives is co-catalyzed by 3-MPA. The observed results indicate that the thiol group adds to the fluorenes carbonyl C-atom. The positively charged intermediate is easily replaced by two phenoxy substituents and 3-MPA is liberated and reused in a next cycle. The reaction is driven by concentrated sulfuric acid, which acts as the main catalyst.

The thiol group of 3-MPA is easily added to the double bond of bicyclopentene. This reaction was also investigated in d6 benzene at room temperature and according to recorded H NMR is a quantitative process. The reaction performs in the dark and therefore no radical mechanism is involved. The reaction is possible due to the remarkable reactivity, which is based on the strain in bicyclopentene.

3-Thiazolines contain a C=N double bond, which perform a ring closure reaction with 3-MPA under azeotropic conditions. The bicyclic product is isolated as a racemate. If R1, R2 carry protons almost no diastereoselectivity (52.5: 47.5) is observed but if R2 is replaced by a isopropyl group a diastereomeric cis-trans ratio 95:5 is found.

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The heterocyclic system 5,6-dihydro-7-1,4,2-oxathiazepin-7-one was prepared by the reaction of hydroxymoyl chlorides with 3-mercaptopropionic acid in a first step. The following ring closure was achieved with 1,3-dicyclohexylcarbodiimide or 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide.

For the telomerization process, 3-mercaptopropionic acid is often used as a chain transfer reagent due to its high transfer reactivity and because the isolated polymer contains a single specific functional end group. AIBN is used as initiator to transform the thiol into a radical. By the variation of the concentration of the chain transfer reagent the telomer length is easily adjusted to a convenient molecular average weight (2000–2500 g/mol). Structures with a lower critical solution temperature are often used for bioconjugates.

References