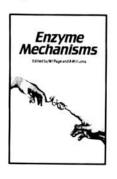
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MANDER'S REAGENT Methyl cyanoformate

1

In 1983, Professor Lewis Mander introduced **methyl cyanoformate** (1) as a reagent which alleviates the frequently encountered problem of competing O-acylation during the C-acylation of ketone enolates. This reagent reacts normally in a highly selective manner with preformed lithium enolates of ketones at the "softer" carbon of the ambident nucleophile affording β -ketoesters almost exclusively under very mild conditions. Since Mander's original report, the reagent has found wide application in organic synthesis and is now familiarly known as **Mander's Reagent**. The following examples highlight its synthetic utility.

Ziegler and co-workers have used **Mander's Reagent** in the synthesis of the insect pheromone (+)-invictolide.

During the synthesis of a griseofulvin analog, Yamato and coworkers observed that acylation performed using ethyl chloroformate yielded mainly O-acylated product, whereas the C-acylated product was obtained in 92% yield when **Mander's Reagent** was employed.³ O

$$\begin{array}{c|c} \text{CI} & \text{OMe} & \text{O} \\ \text{EtO}_2\text{C} & \text{OMe} & \text{OH} \\ \text{MeO} & \text{CI} & \text{CO}_2\text{Me} \\ \text{MeO} & \text{CI} & \text{92}\% \\ \end{array}$$

Speckamp and co-workers employed **Mander's Reagent** for N-acylation of a 2-pyrrolidone derivative, which in turn served as an intermediate in the synthesis of (\pm) -anatoxin, a potent neurotoxin.

Similar reagents such as benzyl cyanoformate and ethyl cyanoformate are also available.

References:

- a) Mander, L.N.; Sethi, P. Tetrahedron Lett. 1983, 24, 5425.
 b) House, H.O. In Modern Synthetic Reactions, 2nd ed.; W.A. Benjamin, Inc.: Menlo Park, 1972; pp 734-816.
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- Yamato, M.; Yoshida, H.; Ikezawa, K.; Kohashi, Y. Chem. Pharm. Bull. 1986 34, 71.
- Speckamp, W.N.; Melching, K.H.; Hiemstra, H.; Klaver, W.J. Tetrahedron Lett. 1986, 27, 4799.
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