Efficient Isomerization for Preparing *trans*-2,2-Dimethyl-3-(2,2-dichloroethenyl) cyclopropanecarbonyl Chloride

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Abstract: *Trans*-2,2-dimethyl-3-(2,2-dichloroethenyl) cyclopropanecarbonyl chloride, which is an important intermediate for insecticides, is obtained by isomerization of the *cis/trans*-mixture with 4- (N,N-dimethylamino) pyridine (DMAP) in the presence or absence of halogen compounds in good yield.

Keywords: Permethric acid chloride; dimethylaminopyridine; conversion.

2,2-Dimethyl-3-(2,2-dichloroethenyl) cyclopropanecarbonyl chloride (hereafter referred to as permethric acid chloride) is a useful intermediate for the preparation of some synthetic pyrethroids, such as permethrin and cypermethrin. Permethric acid chloride has a geometrical isomeric pair, *cis* and *trans*, owing to its cyclopropane ring. It is known that, in general, the esters derived from the *trans*- isomer are less toxic to mammals than those derived from the *cis*- isomer¹⁻³. The permethric acid produced industrially is always in forms of mixtures of *trans*- and *cis*- isomers. Accordingly, it is a problem to convert the *cis*- isomer to the *trans*- isomer, particularly for commercial purpose. One process for the conversion is heating permethric acid chloride at a temperature not lower than 160°C ⁴, while there are some reports dealing with catalyzed conversion of permethric acid chloride, but the *trans:cis* ratio of the final product is not higher than 85:15⁵⁻⁷.

Scheme 1

$$Cl \longrightarrow \underbrace{DMAP/ CH_3CN}_{N_2 \cdot reflux} Cl \longrightarrow \underbrace{Cl}_{C-Cl} Cl \longrightarrow \underbrace{Cl}_{C-Cl} Cl \longrightarrow \underbrace{Cl}_{C-Cl} Cl$$

$$cis/trans-1 \qquad trans-1 \qquad cis/trans-2$$

In this paper, we report a process in which 4- (N, N-dimethylamino) pyridine (DMAP) is used to treat *cis/trans*-mixed permethric acid chloride under mild reaction conditions and in good yield, with a *trans:cis* ratio of 96:4. (**Scheme 1**).

DMAP is added under nitrogen atmosphere to a solution of permethric acid chloride in acetonitrile. The mixture was stirred at 80°C. After the reaction, ethanol is added to the reaction system until esterification is complete. The progress of the reaction can be monitored by gas chromatography or ¹HNMR analysis. The experimental results are summarized in **Table 1**.

Entry 1 catalyst: 1 product 2 catalyst time (trans/cis-%) (mol) (hour) (trans/cis-%) a yield (%) DMAP 60.0/40.0 0.02:1 75.4/24.6 93.2 1 6 2 60.0/40.0 DMAP/Me₄NI 0.02:0.02:1 80.5/19.5 92.8 6 3 60.0/40.0 **DMAP** 0.25:1 6 83.8/16.8 94.7 4 60.0/40.0 DMAP/NaI 0.25:0.08:1 4 86.1/13.9 93.8 5 60.0/40.0 **DMAP** 0.5:1 92.8/7.2 94.9 6 60 0/40 0 DMAP 0.5:1 96.0/4.0 6 95.9 8 60.0/40.0 C_5H_5N 0.5:1 82.3/17.7 90.7 8 60.0/40.0 98.4^{b} 62.0/38.0 8

Table 1. Conversion reaction of *cis/trans-1* to *trans-2*.

Table 1 reveals the following facts. First, the presence of halogen compounds, such as tetramethylammonium iodide or sodium iodide, facilitates the conversion. Second, the molar ratio of catalyst to permethric acid chloride has influence on the *trans/cis* ratio of product **2**. Third, the *trans/cis* ratio of the final product could be raised to 96.0/4.0 at reflux temperature for 8 hours.

The *trans/cis* ratio of the target product **2** is affected by other factors such as solvent, we will discuss it in the near future.

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a) Determined by gas chromatography. b) The crude product is not distilled.