

# The Synthesis of Cinnamoyl Chloride

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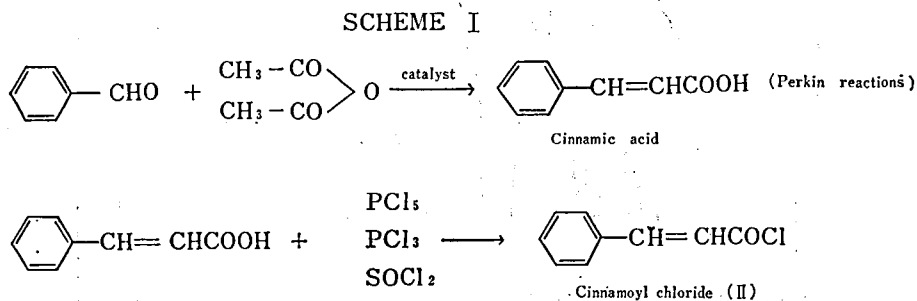
**Abstract:** The reaction of ketene with benzaldehyde, catalyzed by  $\text{BF}_3$ , gave polyester of  $\beta$ -phenyl- $\beta$ -propionolactone(1) in excellent yield. Cinnamoyl chloride(II) was obtained by treating of (I) with thionyl chloride or phosgene, when thionyl chloride was used, in good yield, but with phosgene, in evil yield. In consequence of the yields and reaction conditions of these formations were discussed in comparison with the syntheses, obtained *via* cinnamic acid, starting with benzaldehyde(common methods). This method gave more easily satisfactory results.

## 1. Introduction

As a part of the investigation of the reactions of lactones,<sup>(1)</sup> the reactions of polyester of  $\beta$ -phenyl- $\beta$ -propionolactone with thionyl chloride or phosgene were studied. It has been found that this reaction, when thionyl chloride is used, conveniently gives cinnamoyl chloride in good yield.

Cinnamoyl chloride has recently been used for preparing light-sensitive polymers and vat dyes, the former have been described by Thoma *et al.*,<sup>(2)</sup> Unruh *et al.*<sup>(3)</sup> and Allen *et al.*,<sup>(4)</sup> obtained by treating cinnamoyl chloride with a suitable basic polyamide, polyester, polyurethan, polystyrene or polyvinyl alcohol, and the latter have been described, by Mörgele,<sup>(5)</sup> obtained by condensing cinnamoyl chloride with 4-aminoanthraquinone-1,2-benz-acridone or other anthraquinone derivatives.

In spite of industrially useful product, the synthesis of cinnamoyl chloride has been prepared *via* cinnamic acid from benzaldehyde since old times (Scheme I), therefore, it appears to be interesting to obtain cinnamoyl chloride, without preparing cinnamic acid,

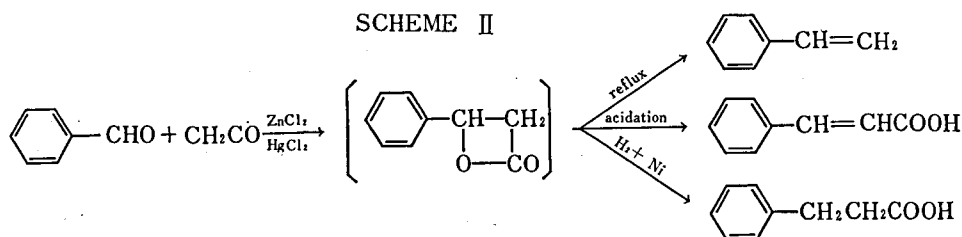


starting with benzaldehyde. On the other hand, the syntheses of cinnamic acid have been reported by many authors, one of the most common methods for synthesis of cinnamic acid is Perkin reactions.<sup>(6)</sup> Cinnmoyl chloride, previously reported by Claisen *et al.*,<sup>(7)</sup> Liebermann<sup>(8)</sup> and H. Meyer,<sup>(9)</sup> is prepared by treating cinnamic acid with phosphorus pentachloride, phosphorus trichloride or thionyl chloride.

## 2. Results and Discussion

### Polyester of $\beta$ -phenyl- $\beta$ -Propionolactone

The reactions of benzaldehyde with ketene, previously reported by Hurd,<sup>(10)</sup> Hagemeyer *et al.*<sup>(11)</sup> and Boese *et al.*,<sup>(12)</sup> give styrene, cinnamic acid or hydrocinnamic acid, without individual separation of  $\beta$ -phenyl- $\beta$ -propionolactone (Scheme II).



Particularly, on a preparing cinnamic acid, described by Boese, after treatment of ketene with benzaldehyde, reaction product is acidified with hydrochloric acid, and cinnamic acid is precipitated, a yield of approximately 42%, based upon the ketene being secured.

While this reaction of benzaldehyde and ketene, catalyzed by  $\text{BF}_3$  at  $0\sim 5^\circ$  for 3 hrs., carried out polymeric viscous liquid, when ether solvent and excess benzaldehyde were removed, unfortunately, did not give  $\beta$ -phenyl- $\beta$ -propionolactone, however, infrared

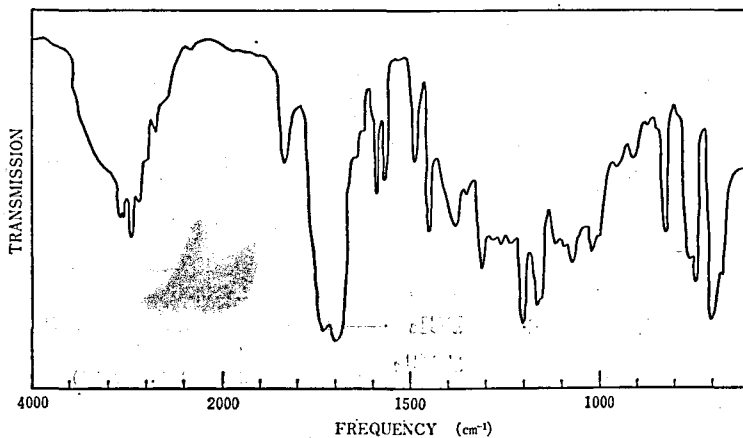


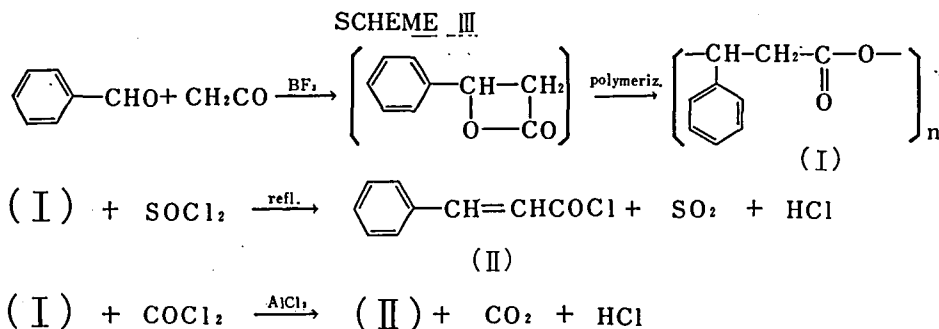
Figure. Infrared spectra of Polyester of  $\beta$ -phenyl- $\beta$ -propionolactone.

spectrum of this liquid displayed major absorption peaks at  $1735\text{ cm}^{-1}$ ,  $1205\text{ cm}^{-1}$  and

1165  $\text{cm}^{-1}$  which are characteristic of ester and at 1830  $\text{cm}^{-1}$  which is characteristic of  $\beta$ -lactone (Shown in Figure). Consequently, it seemed that this reaction gave  $\beta$ -phenyl- $\beta$ -propionolactone at first, and when the  $\beta$ -lactone was heated in order to remove solvent and excess aldehyde, the  $\beta$ -lactone was polymerized, polyester of  $\beta$ -phenyl- $\beta$ -propionolactone was obtained in 90% yield, based upon the benzaldehyde (Scheme III).

### Cinnamoyl Chloride

The reaction of polyester of  $\beta$ -phenyl- $\beta$ -propionolactone with thionyl chloride, at reflux temperature for 5 hrs., gave cinnamoyl chloride in 75% yield, and with phosgene, catalyzed by  $\text{AlCl}_3$ , at 100~134° for 5 hrs., gave cinnamoyl chloride in 6% yield (Scheme III), however, with phosgene, catalyzed by  $\text{AlCl}_3$ , at 1° for 16 hrs., could not give cinnamoyl chloride but gave styrene in a small quantity.



About the problem of the mechanism of these formations, it would be considered that when the polyester was heated, the chain of the polymer was opened, and then chloridation of thionyl chloride or phosgene attacked to carbonyl group of ester. Because, no reaction gave objective product at low temperature, and cinnamic acid, according to a report, is obtained in 42% yield, however, this reaction gave cinnamoyl chloride in 75% yield, therefore, it seemed that this reaction did not give cinnamic acid as intermediate product. Styrene, obtained at low temperature, would be obtained by decarbonator of polyester under distillation. Identity was established by comparison of infrared spectra and retention times of gas chromatographes with methyl cinnamate. For the purpose of comparison with common methods, the author describes about Perkin reactions and about the synthesis of cinnamoyl chloride from cinnamic acid. Perkin reactions are obtained cinnamic acid by treating benzaldehyde with acetic anhydride. These yields and reaction conditions are shown in Table. Cinnamoyl chloride is prepared by treating cinnamic acid with phosphorus pentachloride, phosphorus trichloride or thionyl chloride in good yield (around 90%).

Both methods, to obtain cinnamoyl chloride starting with benzaldehyde, gave similarly satisfactory results, and the yields based upon benzaldehyde were about 67% by this method, when thionyl chloride was used, and 50~72% by common

methods. However, in view of reaction conditions and polyester of  $\beta$ -phenyl- $\beta$ -propionolactone as intermediate product used for next step without purification, in our hands, it gave more easily satisfactory results. In this connection, other unsaturated aromatic acid chlorides will be obtained by the same procedure.

**Table**  
The Syntheses of Cinnamic acid by Perkin reactions <sup>(6)</sup>

Catalyst	Conditions		yield %	Reference
	Temp. c°	Time hr.		
NaOAc	180	8	52	13
KOAc	180	8	64	14
K <sub>2</sub> CO <sub>3</sub>	180	8	59	15
NaOAc C <sub>5</sub> H <sub>5</sub> N	180	8	85	16

### 3. Experimental Section

#### Preparation of Ketene

The Ketene was prepared by pyrolysis of ketene dimer in the manner described by <sup>(17)</sup>Hurd and <sup>(18)</sup>Boese. This ketene dimer was offered by DAICEL Ltd..

#### Reaction of Benzaldehyde with Ketene

Fifty-five grams (1.3 mole) of ketene was passed in through a high speed stirrer in to a solution of 84g. (0.8 mole) of benzaldehyde, 4g. of boron trifluoride and 200ml. of ether in 500ml. -flask, and the flask fitted with a thermometer, a mechanical stirrer, an inlet tube extending nearly to the bottom and an exit tube. While, the reaction mixture was maintained a temperature ranging between 0°and 5°in ice-water bath. After ketene was passed (about 2 hrs. ), the stirring continued for 1 hr. , and the reaction mixture was washed three times with 50ml. of ice-water to remove catalyst, then the solution was dried by magnesium sulfate anhydrous. The ether and excess benzaldehyde were removed by distillation under reduced pressure. Polyester of  $\beta$ -phenyl- $\beta$ -propionolactone was obtained 103g. (90% yield).

#### Reaction of Polyester of $\beta$ -Phenyl- $\beta$ -propionolactone with Thionyl Chloride

One hundred and three grams of polyester of  $\beta$ -phenyl- $\beta$ -propionolactone and 124g. (1 mole) of thionyl chloride were placed in a 500ml.-claisen flask, and the flask was connected with a reflux condenser, and to the top of the condenser was attached an exit tube, for evolved hydrogen chloride and sulfur dioxide, leading to a gas-absorption trap.

The reaction mixture was heated on a steam bath, until no further evolution of hydrogen chloride was noted, and then excess thionyl chloride was removed by distillation. The residue was distilled at reduced pressure. Cinnamoyl chloride was collected at 86°/1.7mm., and yielded 87g. (75%).

#### Reaction of Polyester of $\beta$ -Phenyl- $\beta$ -propionolactone with Phosgene

Fifty grams of polyester of  $\beta$ -phenyl- $\beta$ -propionolactone, 50g. (1/2 mole) of phosgene and 2g. of aluminum chloride anhydrous were placed in 100ml.-autoclave. The reaction mixture was heated cautiously at first, and maintained range between 100° and 134° for 5hrs., and then the mixture was cooled, and filtered. The filtrate was distilled at reduced pressure. Cinnamoyl chloride was obtained 5g. (6% yield).

#### Acknowledgment

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