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Catalytic Dimerization of Ketene
A Simple and Convenient Method for the Preparation of Diketene and Esters of Acetoacetic Acid

Short Communication

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A new method for the preparation of diketene is described. The main feature of the procedure is the dimerization of ketene in the presence of tetramethylethylenediamine (*TMEDA*) and the direct use of crude diketene in the syntheses of acetoacetic esters.

(Keywords: Dimerization of ketene; Tetramethylethylenediamine, catalytic action of)

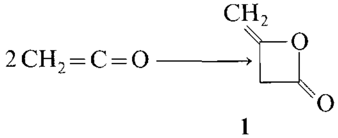
Katalytische Dimerisierung von Keten. Eine einfache und praktische Methode zur Darstellung von Diketen und Estern der Acetoessigsäure (Kurze Mitteilung)

Es wird eine neue Modifikation bei der Herstellung von Diketen beschrieben. Das wesentliche an der Methode ist die Gegenwart von Tetramethylethylendiamin (*TMEDA*) bei der Dimerisierung von Keten und der direkte Einsatz von rohem Diketen bei der Synthese der Acetoessigsäureester.

Diketene (**1**) is mainly prepared by the non-catalytic dimerization of ketene[1].

The procedure is long and troublesome because of the low reaction rate[2]. Tertiary amines, as kinetic measurements showed[3], catalize the dimerization of ketene but so far this fact has found no practical application. Attempts to use pyridine as a catalyst proved to be unsuccessful because of the formation of by-products[4].

In the search for a simple method of preparation of diketene we found[5] that by passing ketene through a 0.1% hexane solution of tetramethylethylenediamine (*TMEDA*) at − 10 to − 15 °C the dimerization of ketene proceeds quickly. Crude diketene is only little soluble in hexane and separates during the reaction, forming the lower layer. This fact probably limits the consecutive dimerization of diketene to dehydroacetic acid. The latter reaction proceeds very easily in the presence of tertiary amines[6] and therefore the crude diketene is unstable at room temperature. It should be either immediately subjected to further reactions with suitable reagents or stored in dry ice. Crude diketene obtained by this procedure can also be purified by distillation under reduced pressure after the addition of *p*-toluenesulfonic acid, which increases its stability.



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$$\mathbf{1} + \underset{\mathbf{2}}{R\mathrm{OH}} \longrightarrow \underset{\mathbf{3}}{CH_3COCH_2CO_2R}$$

The crude diketene is sufficiently pure to be used directly for the preparation of esters of acetoacetic acid. This can be accomplished simply by refluxing the mixture of crude diketene with an appropriate alcohol without adding any catalyst usually required in this type of reaction[7] (Table 1).

Other catalysts have been used in the preparation of diketene: *p*-toluenesulfonic acid in *N*-methyl-2-pyrrolidone or butyrolactone[9] and potassium acetate in acetone[10]. These methods are, however, inconvenient because either expensive solvents are used or the reaction requires a long time (12–15 h) at low temperatures (dry ice!).

Table 1. *Esters of acetoacetic acid* (**3**) *prepared*

Product No.	*R*	Yield[a] %	b. p. °C/Torr found	b. p. °C/Torr reported
3a	CH_3	72.5	72°/18	68°/12[8]
3b	$(CH_3)_3C$	75.0	70–71°/10	72–73°/10[8]
3c	$PhCH_2$	65.6	155–157°/10	156–159°/10[8]
3d	$CH_2{=}CHCH_2$	72.3	91–92°/20	93°/21[8]

[a] Yield from ketene.

Our method of preparation of diketene, in which *TMEDA* is used, simplifies the procedure in comparison with known methods: it takes less time, gives a good yield of the product and is especially advantageous when diketene is further used in acetoacetic esters synthesis.

Experimental

Ketene gas was prepared by the pyrolysis of acetone by passing it through a quartz tube packed with copper wire and heated to 760 °C[11].

Diketene (**1**)

Three 300 ml gas-washing cylinders were connected in series. The second and third cylinders were equipped with an inlet tube ended with a sintered head and charged with a solution of 0.04 g of *TMEDA* in 60 ml of hexane. The first cylinder was installed in order to remove the unreacted acetone. All the cylinders were cooled to − 10 to − 15 °C and ketene gas (0.73 mol per h) was passed through them for 3.5 h. The content of the cylinders was collected and the dark brown lower layer separated in a separatory funnel. The crude product, which consists of diketene, hexane, acetone and non-volatile material was purified by vacuum distillation after adding 0.5 g of *p*-toluenesulfonic acid. Most of the solvents were removed at room temperature under the pressure of 60 Torr. The system was then evacuated to 45 Torr and a colourless liquid was collected at 52–53 °C (lit. 50.5 °C/41 Torr[8]). The yield of pure diketene was 78.8 g (75%).

Alkyl Acetoacetates (**3**) *(General Procedure)*

The collected content of the two washing-cylinders was placed in a 1 000 ml round-bottom flask, 3 mol of an appropriate alcohol **2** was added and the mixture refluxed for 4.5 h. The mixture was cooled to room temperature and evaporated using a rotary evaporator. The residue was distilled under reduced pressure.

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