

7. Reaction of Ketene with Ethylacetoacetate in the Presence of Some Organic Bases

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In the previous paper (This Bulletin, **31**, 382(1953)), it was reported that ketene reacts with ethylacetoacetate to give C-acetyl derivative $\text{CH}_3\text{COCHCOOC}_2\text{H}_5$ or O-acetyl derivative $\text{CH}_3\text{C}(\text{OCOCH}_3)=\text{CHCOOC}_2\text{H}_5$ according to the reaction conditions.

Some organic bases, i. e. dimethylaniline, quinoline, pyridine, triethylamine and piperidine accelerated the reaction of ketene with ethylacetoacetate.

With these catalysts, O-acetylation occurred mainly when the reaction was carried out under cooling with ice, but C-acetylation predominated when they reacted under warming on a steam bath.

Pyridine alone, however, gave the product rich in O-acetyl derivative, even under warming.

It seemed that there is no relation between K_B of the bases and the reaction types. The results of experiments are summarized in the table on page 36.

8. Reactions of Ketene with Compounds Containing Active Methylene Hydrogen

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It was already reported that the reaction of ketene with ethylacetoacetate or its sodium salt gave C-acetyl derivative in the absence of catalyst, and in the presence of sulfuric acid, O-acetyl derivative was sole product (This Bulletin **31**, 382 (1953)).

There is no information about the formation of C-acetyl derivatives in the reaction of ketene with *compounds containing active methylene hydrogen* (henceforth abbreviated as *compds. cont. A. M. H.*).

Now, in our experiments, ketene and some *compds. cont. A. M. H.*, i. e. acetylacetone, ethylmalonate, ethylcyanoacetate and malononitrile as well as ethylacetoacetate, gave C-acetyl derivatives or O-acetyl derivatives, according to the reaction conditions.

The results obtained are as follows :

(1) Without catalyst, acetylacetone and ethylacetoacetate gave C-acetyl derivatives whereas the others failed to react.

(2) All the sodium salts of the compds. cont. A. M. H. mentioned above gave C-acetyl derivatives.

(3) In the presence of sulfuric acid, acetylacetone and ethylacetoacetate produced O-acetyl derivatives while the others did not react.

Table 1. Reactions of ketene with compounds containing active methylenic hydrogen.

Catalyst	React. Temp. ¹⁾	Comps. Cont. A. M. H. Products	$\text{H}_2\text{C} \begin{matrix} \diagup \text{COCH}_3 \\ \diagdown \text{COCH}_3 \end{matrix}$	$\text{H}_2\text{C} \begin{matrix} \diagup \text{COCH}_3 \\ \diagdown \text{COOC}_2\text{H}_5 \end{matrix}$	$\text{H}_2\text{C} \begin{matrix} \diagup \text{COOC}_2\text{H}_5 \\ \diagdown \text{COOC}_2\text{H}_5 \end{matrix}$	$\text{H}_2\text{C} \begin{matrix} \diagup \text{CN} \\ \diagdown \text{COOC}_2\text{H}_5 \end{matrix}$	$\text{H}_2\text{C} \begin{matrix} \diagup \text{CN} \\ \diagdown \text{CN} \end{matrix}$
			Name ²⁾³⁾	C	×	—	—
None	Low	Name ²⁾³⁾	C	×	—	—	—
		Conv. ratio (%) Yield ⁴⁾ (%) I. II.	52 31 61				
	High	Name	C	C	×	×	×
		Conv. ratio (%) Yield (%) I. II.	76 61 80	43 37 86			
Na-Slat ⁵⁾	Low	Name	C	C	C	C	C(?) ⁶⁾
		Conv. ratio (%) Yield (%) I. II.	40 8 20	100 55 55	35 18 51	50 10 20	
	High	Name	—	C	C	C	—
		Conv. ratio (%) Yield (%) I. II.		98 57 58	58 20 34	43 13 30	
conc. H ₂ SO ₄	Low	Name	O	×	—	—	—
		Conv. ratio (%) Yield (%) I. II.	40 34 85				
	High	Name	O	O	×	×	×
		Conv. ratio (%) Yield (%) I. II.	60 22 37	85 67 79			
Pyridine	Low	Name	O	O (rich) C (poor)	—	—	—
		Conv. ratio (%) Yield (%) I. II.	32 22 69	32 26 81			
	High	Name	O (rich) C (poor)	O (rich) C (poor)	C (trace)	C	C(?) ⁶⁾
		Conv. ratio (%) Yield (%) I. II.	48 28 59	52 40 77		19 9 47	

- (1) Reaction temperature: Low—cooling with ice (0-10°C);
High—warming on a water bath (60-90°C).
- (2) C: C-acetyl derivative of the compd. cont. A. M. H.
O: O-acetyl derivative of the compd. cont. A. M. H.
- (3) ×: No reaction.
- (4) Yield I: Yield based on the compd. cont. A. M. H. used.
II: Theoretical yield.
- (5) Na-salt: Treated with 20 % H₂SO₄ after the reaction of ketene with the salt of the compd. cont. A. M. H.
- (6) C(?): Not identified.

(4) With pyridine, a product rich in O-acetyl derivative and poor in C-acetyl derivative was obtained from acetylacetone or ethylacetoacetate, but it seemed the others gave solely C-acetyl derivatives.

The data of experiments and some physical constants of C-acetyl derivatives are summarized in Tables 1 and 2.

Table 2. Some physical constants of C-acetyl derivatives obtained from the compounds containing active methylenic hydrogen.

C-acetyl derivative	Physical properties		
	B. P. (°C)	<i>n</i> _D	M. P. of Cu-salt (°C)
CH ₃ COCH $\begin{cases} \text{COCH}_3 \\ \text{COCH}_3 \end{cases}$	100-102 (20mm)	1.4872 ¹⁶	decomp. (192-195)
CH ₃ COCH $\begin{cases} \text{COCH}_3 \\ \text{COOC}_2\text{H}_5 \end{cases}$	102-104 (20mm)	1.4710 ¹⁵	150-1
CH ₃ COCH $\begin{cases} \text{COOC}_2\text{H}_5 \\ \text{COOC}_2\text{H}_5 \end{cases}$	125 (14mm)	1.4469 ¹³	122-3
CH ₃ COCH $\begin{cases} \text{CN} \\ \text{COOC}_2\text{H}_5 \end{cases}$	106-111 (20mm)	1.4488 ²³	234-5

9. Reaction of Ketene with Acetone

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In the reaction of ketene with acetone, β,β -dimethylacrylic acid $\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} > \text{C} = \text{CHCOOH}$ was obtained, when catalyzed with BF₃ and in the presence of conc. H₂SO₄, isopropenylacetate $\begin{matrix} \text{CH}_3 \\ \text{CH}_2 \end{matrix} > \text{COCOCH}_3$ was produced. However, ketene did not react with sodium salt of acetone to give acetylacetone.

Some results of the experiments are as follows:

(1) Fifty grams of ketene was passed during 100 minutes into a solution of 1 g. of BF_3 in 58 g. of acetone at 0°C . Without removing BF_3 , the product was distilled to give 32 g. of β,β -dimethylacrylic acid. Under similar conditions, using $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{BF}_3$ or $(\text{CH}_3\text{CO})_2\text{O}\cdot\text{BF}_3$ as catalyst, 10 g. or 21 g. of β,β -dimethylacrylic acid was obtained.

With AlCl_3 or ZnCl_2 , β,β -dimethylacrylic acid was not gained at all and the high polymers of ketene seemed to be produced. In the presence of ZnCl_2 , a small amount of dehydroacetic acid was obtained.

(2) Forty two grams of ketene was passed into a solution of 116 g. of acetone and 1 g. of conc. H_2SO_4 at about 50° . The product was fractionated to give 28 g. of isopropenylacetate. From a reaction of 59 g. of ketene, 87 g. of acetone and 1 g. of conc. H_2SO_4 , 30.5 g. of isopropenylacetate was obtained.

(3) On treating the reaction product with 20 % H_2SO_4 after the reaction of ketene with sodium salt of acetone was finished, acetylacetone was not obtained and pinacol-like substance was found, but it was not studied further.

10. Mechanism to Improve the Crease Recovery of Fabrics by the Resin Treatment

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The degree of the crease recovery of fabrics, especially that of the spun rayon fabrics, is remarkably improved by the urea formaldehyde resin treatment, but in many cases, the degree of elasticity (elastic recovery) of the single fiber does not change so much as the crease recovery of the fabric. To make clear this relation, the degree of elasticity of the single fiber taken out from the resin treated spun rayon Serge and rayon Habutae was compared with the crease recovery of these fabrics. Moreover the degree of elasticity of the single fiber and zigzag-formed rayon yarn¹⁾, and the crease recovery of the spun rayon Muslin, which have been treated by urea resin in various conditions, were estimated. From these results, it was found that the change of the degree of elasticity of the single fiber was small, but the degree of elasticity of zigzag-formed yarn and the crease recovery of the fabric remarkably increased almost in the same degree.

It is presumed that the recovery of deformation of the zigzag form of yarn constructing the fabric plays the main part to improve the crease resistance of fabrics by the resin treatment.

Following table gives some of the results obtained.