

## 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.

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## 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.