

THE ACYLOIN CONDENSATION. IV. AVOIDANCE OF
DIECKMANN CONDENSATION PRODUCTS IN ACYLOIN CONDENSATIONS

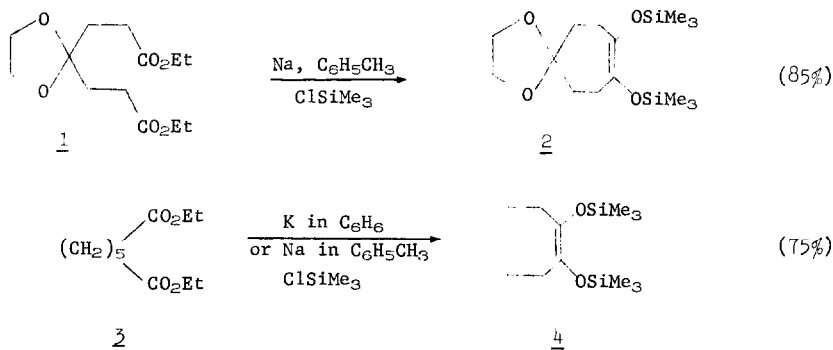
Jordan J. Bloomfield (1)

Central Research Department, Monsanto Company,
Saint Louis, Missouri 63166

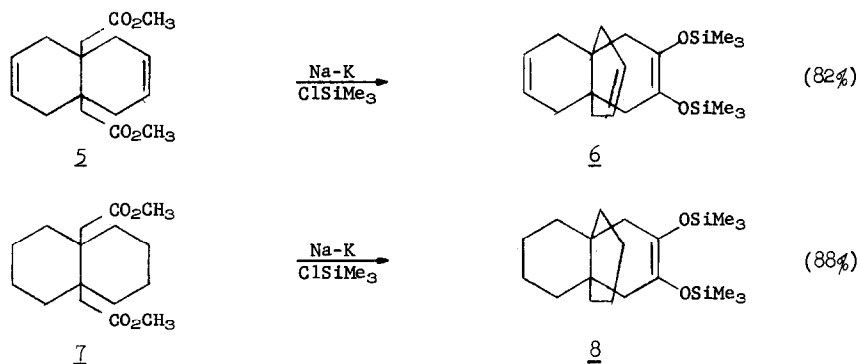
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In the preceding paper in this series (2) successful acyloin condensations of 1,2-diesters to cyclobutane derivatives were described. The key to these syntheses is the introduction of chlorotrimethylsilane into the reaction mixture. The silane acts as a scavenger for all alkoxides producing alkylsilyl ethers and sodium chloride, while the reaction mixture remains neutral.

In cases where the acyloin reaction is slow or when competing base catalyzed reactions are very fast, the presence of alkoxide can lead to Claisen and Dieckmann condensations. Instances where the Dieckmann condensation does compete successfully with the acyloin condensation have been summarized (3). Of the examples described in ref. 3 the ketal, 1, which is reported to give only the Dieckmann product (4,5) and diethyl pimelate, 3, which gave a mixture of Dieckmann and acyloin products (4) are readily obtained. For this reason, they were chosen as models to see if addition of chlorotrimethylsilane could inhibit the Dieckmann condensation. The results shown below indicate that this modification is very successful.



These experiments, coupled with our interest in propellanes (6), led us to use the new conditions in cyclizations of the diesters 5 and 7. Attempted cyclization of these esters, using an excess of sodium-potassium alloy (7), in the absence of the chlorosilane, was only partially successful. A mixture of several components was obtained from which crystalline material was not obtainable. Under the same conditions, but in the presence of the silane, a very good yield of acyloin products was obtained (8).



The reactions required 2 - 3 days, which is more than sufficient time for the alkoxide formed in the reaction (if not scavenged) to bring about the Dieckmann condensation (9).

The results reported here and in the previous paper (2) prompt us to suggest that all acyloin condensations (particularly in cases where the mechanism of the reaction is being investigated) ought to be carried out in the presence of a base scavenger; e.g. chlorotrimethylsilane.

It is important to note here that the cyclization products may be readily hydrolyzed in good yield to the acyloin (10).

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