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# THE RELEVANCE OF ESTER EXCHANGE IN OXALACETIC ESTERS TO THE DECARBONMONOXYLATION REACTION[1]

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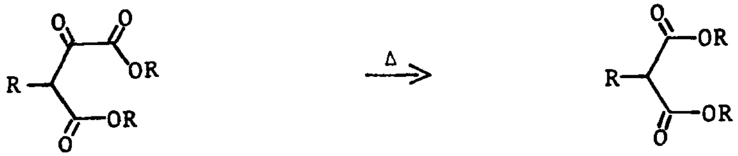
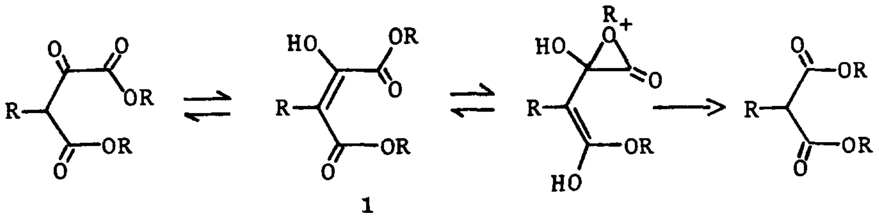
Summary: Oxalacetic esters undergo ester exchange at 120° C, at which temperature loss of CO does not occur. A new mechanism is proposed for the decarbonmonoxylation reaction.

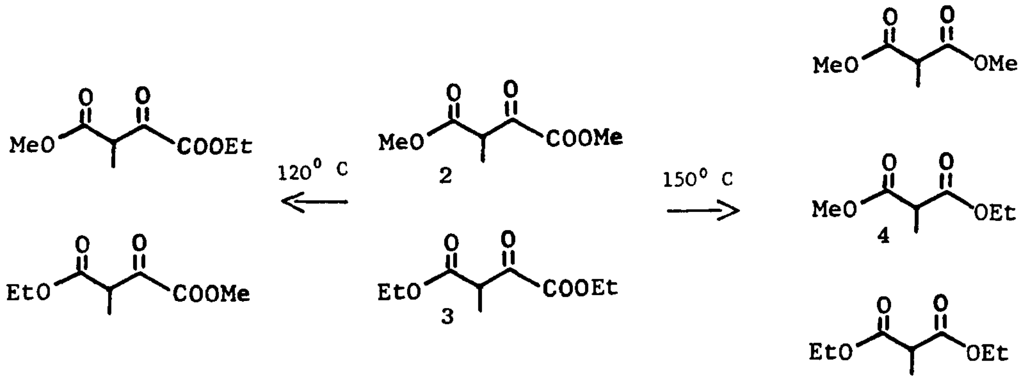
The conversion of oxalacetic esters to malonic esters was exploited as early as 1894,[3] and remains a useful and well documented procedure.[4] Yet little is known of the mechanism of this venerable reaction. In 1924 D. L. Watson discovered that the reaction was unimolecular[5] and many years later it was shown that the traditional catalysts were unnecessary.[6] It was noted in 1968[7] that the known[8] high temperature (850-880° C) conversion of oxalacetates to carbon suboxide did not involve a symmetrical heteryne, but no comment was made about the low temperature process. The most significant observations were made in 1959 when Banholzer and Schmid found that dialkylation effectively stopped the reaction although a variety of monosubstituted molecules successfully yielded malonic esters.[6] These authors also proved that it was the pyruvate ester carbonyl group that was lost as carbon monoxide. These facts were incorporated into a suggested mechanism based on the formation of enol 1, which was thought to rearrange in intramolecular fashion.[6] Although the information provided by Banholzer and Schmid went far beyond what had gone before, the main virtue of their mechanism seems to be that it predicts the loss of the correct carbonyl group.



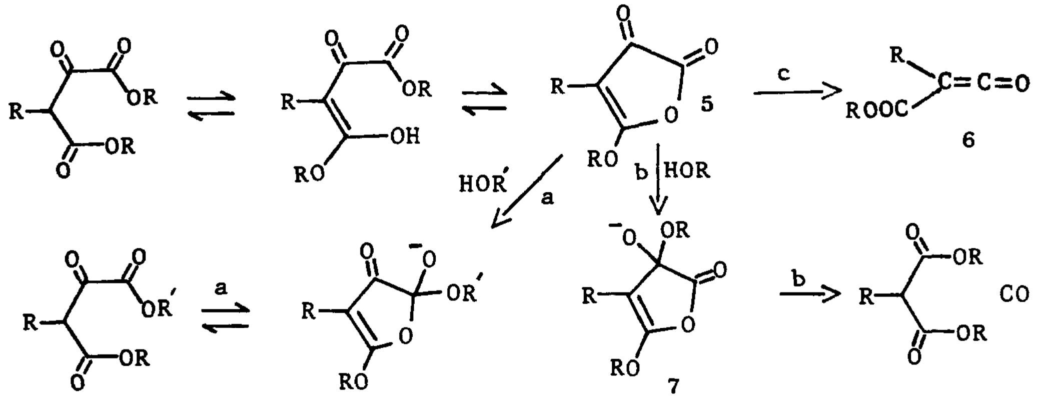


The related thermal loss of carbon monoxide from pyruvic esters is even less well understood. Here debate continues not only on the role, if any, of catalysts, but on the very existence of the reaction. Calvin and Lemmon reported the facile formation of methyl acetate from methyl pyruvate in 1947,[9] and showed that here, too, it was the ester carbonyl that was lost. Louw and Kooyman repeated the reaction in 1967, albeit at much higher temperature and in the gas phase.[10] However, the pyrolysis of other pyruvates takes a different course,[10,11,12] and we[13] and others[12] have been unable to repeat the earlier work of Calvin and Lemmon.[9]

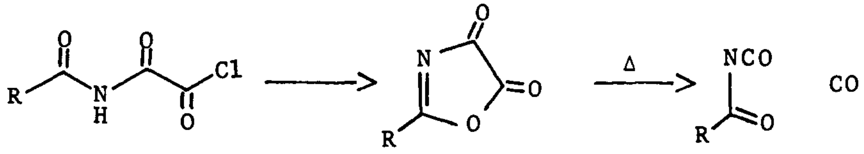
We have discovered that oxalacetic esters undergo ester exchange at temperatures (*ca.* 120° C) below that at which they lose carbon monoxide (*ca.* 150° C). Thus a co-pyrolysis of 2 and 3 at 150° C led to the mixed ester 4 as required by an intermolecular process, and at 120°C 2 and 3 exchange much faster than they give malonic esters. The earlier mechanism[6] cannot explain this exchange which suggests the presence of free alcohol. We have verified that oxalacetic esters do exchange when heated with alcohols at the reaction temperature, and have been able to trap free alcohol with added phenyl isocyanate.



We suggest oxobutenolide 5 as the active ingredient in both the exchange reaction and the formation of malonic esters. This requires that enolization take place in the "wrong" direction, but there is ample precedent for such a counter-thermodynamic process being productive in a chemical reaction.[14] Once formed, 5 can be attacked at both carbonyl groups with path ("a") leading to exchange.



Reactions related to our postulated mechanism are known, yet, to our knowledge, their relevance to the decarbonmonoxylation of oxalacetic esters has not been remarked. Speziale and co-workers have thoroughly investigated the formation of acyl isocyanates through the reaction of amides with oxallyl chloride and have shown that a mechanism much like the one postulated above obtains.[15] Thio amides give thioacyl isocyanates.[16]



There are many furanediones related to our postulated 5 in the literature, largely due to the work of Kollenz.[17,18] Moreover, they have been shown to lose carbon monoxide to form trappable ketenes,[17,18] or, in related cases,[16] stable isocyanates, at temperatures comparable to those required for the decarbonmonoxylation of oxalacetic esters. The last step of our mechanism may also involve ketene formation (path "c") although the very high yield of malonate argues against the presence of a sensitive intermediate such as 6. Alternatively, attack along path ("b") may be accompanied by loss of carbon monoxide directly from 7.

Our many failures to isolate 5 may reflect either our lack of experimental skill or the relative thermodynamic instability of this intermediate.

## REFERENCES AND NOTES

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(2) Portions of this work are taken from the A.B. Theses of A.L.F. (1977), S.D.G. (1981) and R.S.S. (1985), Princeton University. Conversations with Prof. Robert A. Pascal were especially helpful. We also thank Dr. David Williams for pointing out reference 18.

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