Tetrahedron Letters No. 1, pp 79 - 80, 1975. Pergamon Press. Printed in Great Britain.

INTERCONVERSIONS OF β-DICARBONYL ANIONS THROUGH ACTIVATED CYCLOPROPANES

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(Received in USA 8 November 1974; received in UK for publication 25 November 1974)

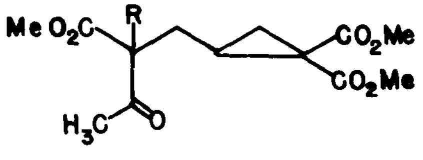
Recently we described the base induced transformation of the β-ketoester 1 to the dihydrofuran 2[1] by intramolecular homoconjugate attack of the ambident β-ketoester anion, 1a. Previously[2] we had reported the interconversion of esters 3 and 4 via equilibration of their anions.

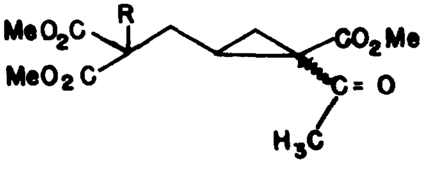
It was thus of interest to determine whether equilibration between 1a and 5a might be occurring concurrently with formation of the dihydrofuran. One way in which this question might be probed would be to examine the consequences of starting with 5. Accordingly, dimethyl allylmalonate was subjected to cyclopropanation with methyl diazoacetoacetate[3] (a solution of 0.05 mole of olefin and 0.05 mole of diazocompound was added, slowly to a mixture of 0.05 mole of olefin and 200 mg of copper bronze heated at 140°). A 13% yield of system 5 (cis and trans isomers, δCCl_4 MeCO = 236 and 240 cps) was obtained in analytically (Found C, 54.36, H, 6.40%) pure form.[4]

Treatment of 5 with sodium hydride in benzene for 15 hr at rt gave a 78% yield of dihydrofuran 2 These conditions are too mild for a simple cyclopropyl ketone → dihydrofuran rearrangement.[5] A more likely pathway starts with fluxional conversion of 5a → 1a followed by intramolecular O-alkylation of the latter anion. Strong presumptive evidence in favor of this interpretation, was obtained by analysis[6] (t l.c.) of the reaction mixture at intermediary stages. Quenching after 5 min shows the formation of small amounts of 1 After 1.5 hr, a 1:1:1 mixture of 5, 1 and 2 is produced. While it has not been demonstrated in rigorous kinetic terms, the pathway 5a → 1a → 2a seems beyond question.

We have re-investigated the process starting with 1. Treatment of 1 with sodium hydride-benzene affords, after workup, the dihydrofuran 2. Examination of aliquots at intermediary stages, fails to reveal the presence of discernible (t.l.c.) amounts of 5. While we can not rule out the presence of small amounts of 5, the predominant anion must certainly be 1a. Since it is unlikely that the difference in stability between 1a and 5a is due to any steric effects, or to any significant differences in conjugation of a cyclopropane ring with two esters as opposed to one ester and one acetyl group, we ascribe it to the greater acidity of a β-keto-ester relative to a malonate.[7] To our knowledge, this represents the first case where this stability order has been so clearly demonstrated in a competitive intramolecular situation.

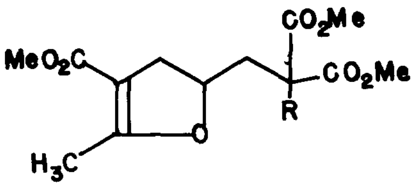
Acknowledgment - This research was supported by P.H.S. Grant CA 12107-10.





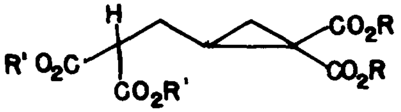
1 R = H $\overset{?}{\dashrightarrow}$ **5** R = H

1a R = Na $\longleftarrow$ **5a** R = Na



2 R = H

2a R = Na



3 R = Me; R' = Et

4 R = Et; R' = Et

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4. For an intramolecular version (55% yield) of cyclopropane formation from diazoacetoacetates see G. Cannic, G. Linstrumelle and S. Julia, Bull. Soc. Chim. France, 4913 (1968), To our knowledge this case, albeit in low yield is the first intramolecular example.
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6. Compound 1 and 5 were not stable to gas chromatography.
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