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CLAY CATALYZED ENE-REACTIONS. SYNTHESIS OF γ-LACTONES

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Summary : The ene-reaction of olefins with diethyloxomalonate is catalyzed by kaolin or K10 montmorillonite. The ene-reaction products are converted into γ-lactones, especially by montmorillonite.

Ene-reactions occur generally at high temperature. Lewis acid catalysis allows ene-reactions under mild conditions.[1]

Clays may catalyze chemical reactions by acting as Brφnsted acids or Lewis acids : isomerizations [2], dimerizations [3], acetal [4], ester [5a] and ether formation [5b,6,7] have been performed with clay catalysts. Clay supported reagents have been used for oxidation [8] or Diels-Alder reactions [9].

We have studied the kaolin and montmorillonite catalyzed ene-reactions.

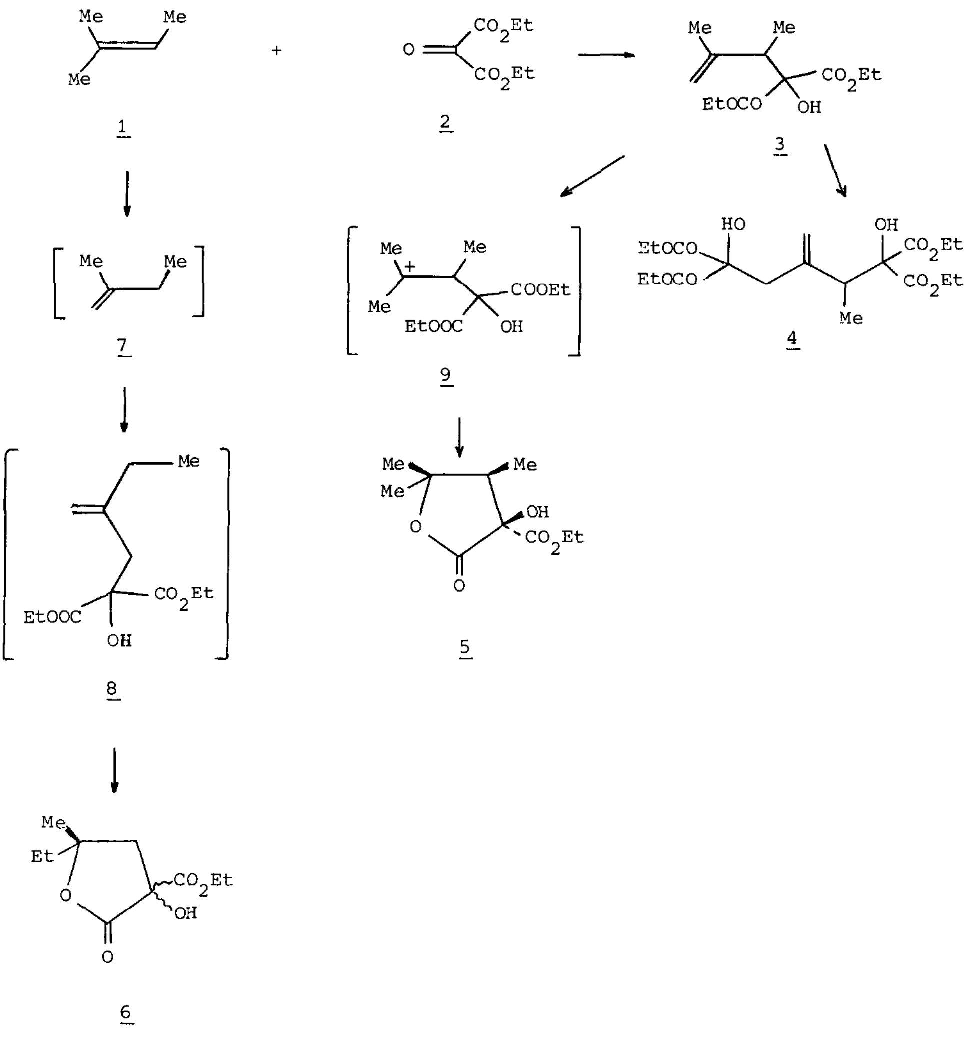
Diethyl oxomalonate 2, which is a very reactive enophile,[10] was treated with 2-methyl 2-butene 1. The kaolin catalyzed reaction occured at 70-90°C and gave the ene products 3, 4 and the lactone 5 (only one diastereoisomer). The yield of 5 was increased when the reaction time was higher (table I). Compound 4 was formed by a secondary ene-reaction on the product 3 (scheme I).

The ene-reaction catalyzed by K10 montmorillonite gave solely the lactones 5 (only one diastereoisomer) and 6 (two diastereoisomers, in the ratio 50 : 50). The lactones 6 arise from the isomerization of 2-methyl 2-butene (1) into 2-methyl 1-butene (7).

The ene adduct 8 from the reaction of 7 with 1 was converted into the lactones 6. The crystalline diethyloxomalonate hydrate 10 gave the same reactions than 2.

No reaction was observed when diethyloxomalonate and 2-methyl 2-butene 1 were heated at 90°C for 48 h, in the absence of the clay.

The lactones 5 and 6 were easily separated by flash chromatography (silica gel) with ether/petroleum ether (1/1) as eluent. The ene adduct 4 was isolated by simple short-path distillation from the ene-reaction mixture. The ene adduct 3 and the lactone 5 were separated by flash chromatography on silica gel (petroleum ether/ether 1/1 as eluent).



Scheme I

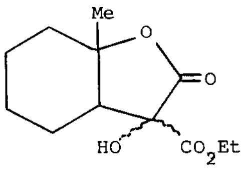
Structural assignments of 3 - 6 were based on spectral data (^1H and ^{13}C NMR, mass spectrometry).

The structure of the isomer 5 (Z) was established by NMR spectroscopy, by addition of the shift reagent Eu(fod)$_3$.

The observed ene reactions were regiospecific. Kaolin did not lead to double bond migration. The formation of the γ-lactone 5 was stereoselective.

At the temperature used, clays act essentially as Brønsted acids (6). The use of an montmorillonite doped with Fe^{III} [9,11] did not improve the yields of γ-lactones.

This synthesis of lactones can be extended to simple alkenes. The K10 montmorillonite catalyzed ene-reaction of 1-methyl cyclohexene with diethyl oxomalonate, at 80° for 48 h, gave the lactones 11 (37 %) and 12 (23 %). In the same conditions, cyclohexene gave the lactone 13 (two diastereoisomers, 25 %).



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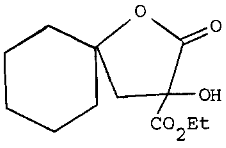

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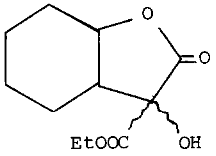

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In conclusion, a simple procedure for the synthesis of γ-lactones is presented. The major advantages is the relative ease with which this procedure is conducted, without dry solvent and with less expensive catalyst than those used previously. The scope of these reactions is now explored.

Table I - Reaction of 2-Methyl 2-butene with Diethyl oxomalonate.

Reaction conditions [a]			Yield [b]	Product distribution, % [c]				
Catalyst	Temp, °C	Time, h	%	2[d]	3	4	5	6
Kaolin	72	19	82	59	37	0.5	3	
Kaolin	125	19	82	29	63	2	5	
Kaolin	90	120	78	26	5	19	49	
Montmorillonite	80	72	78	7			49	44

[a] A mixture of 2g of catalyst, 15 mmol of 1, 10 mmol of 2 was heated for the time indicated.
[b] Sum of isolated yields of all components based on 2.
[c] Determined by GLC before purification.
[d] 2 was recovered as hydrate.

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