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$Ba(OH)_2$ AS CATALYST IN ORGANIC REACTIONS-PART XVI-CONTRIBUTION TO THE STUDY OF THE MICHAEL ADDITION MECHANISM TO CHALCONE IN INTERFACIAL SOLID-LIQUID CONDITIONS

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Abstract.-The Michael addition of several active methylene compounds to chalcone,catalyzed in interfacial solid-liquid conditions is described.The mechanism of the process is analyzed using the Michael addition of diethyl malonate to chalcone as the reaction test.Several microcrystalline barium hydroxide catalysts are tested.The nature of the solid catalyst active sites taking part in the process is discussed.The presence of the adsorbed carbanion from the malonate-on the strong basic site of the solid-is shown by IR spectroscopy.A Merifield resin is used to prove that the process takes place on the solid surface.

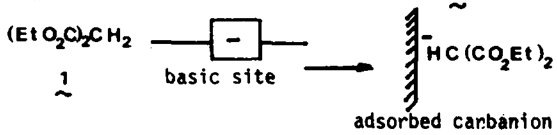
Michael addition is a general synthetic method to create carbon-carbon bonds in mild conditions[1-4]. The regioselectivity of the process (1,2- versus 1,4-addition) is controlled by the temperature,the the nature of the solvent,catalyst[5] etc.Nevertheless,Michael addition in classic experimental conditions has some disadvantages such as secondary reactions due to the basic character of the catalysts.These disadvantages can be avoided using Phase Transfer Conditions.Some catalysts have been used such as $:F^-$ in the presence of ammonium salts[6-8],solid bases in the presence of phase transfer catalysts[9],KF/Al_2O_3[10] etc.

The mechanism of Michael addition has been studied with several kinds of homogeneous catalysts e.g:amines,alcohoxides and hydroxides[11,12] not however in interfacial solid-liquid conditions (Experimental ones used more and more by organic chemists).

Some time ago we described an activated barium hydroxide catalyst,C-200,which is very active as the catalyst in many organic reactions e.g:the Claisen-Schmidt condensation[13];the Wittig-Horner reaction[14];the synthesis of coumarinic compounds[15]; Δ^2-pyrazolines and Δ^2-isoxazolines[16] etc.

In the present paper we compare the catalytic activity of C-200 with that of other barium hydroxide catalysts(C-300 and C-0) with different microcrystalline structures and,therefore with different amounts of active sites in order to get information on the interfacial mechanism.The Michael addition of diethyl malonate,1,to chalcone,2,was used as the reaction test for the simple experimental conditions.

Similar to the mechanism described for aldol condensation[17] or the Wittig-Horner reaction[18] catalyzed by C-200 in interfacial solid-liquid conditions,we could postulate a two step mechanism.
1st. step.-adsorption and formation of carbanion from 1 on the active site



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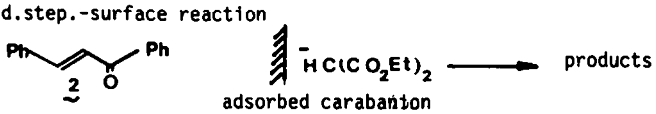
2nd.step.-surface reaction



This mechanism is confirmed,at a qualitative level,by the results in the paper

RESULTS AND DISCUSSION

1.-Catalysts

The interfacial solid-liquid reactions catalyzed by microcrystalline insoluble solids are concontrolled by the structure of active sites by means of their geometric,electric and acid-base characteristics[17,19].Therefore a complete structural analysis has been carried out[20].The results are summarized in table 1 and 2.

Table 1

Chemical and textural properties of catalysts

	C-0	C-200	C-300
Surface area (m^2/g)	1.4 ± 0.1	1.9 ± 0.1	1.4 ± 0.1
Number of active sites (mmol.ads/g.cat.),versus			
TBMPHE (pKa=11.7)	$(2.6 \pm 0.3)\ 10^{-2}$	$(6.3 \pm 0.2)\ 10^{-3}$	$(2.2 \pm 0.1)\ 10^{-3}$
BA (pKa=4.2)	$(5.5 \pm 0.6)\ 10^{-1}$	$(9 \pm 1)\ 10^{-2}$	$(6.0 \pm 0.6)\ 10^{-2}$
DNB (E.A.=2.21 e.V.)	$(5.5 \pm 0.6)\ 10^{-2}$	$(3.5 \pm 0.4)\ 10^{-2}$	$(0.7 \pm 0.07)\ 10^{-3}$
Cyclohexylamine(pKa=10.6)[a]	-	-	-
Pyridine (pKa=5.3)[a]	-	-	-
Phenothiazine(I.P.=7.31 e.V.)[a]	-	-	-

[a] No adsorption of the reactive by the solid is observed

The low surface area values (Table 1) are due to the microcrystalline structure of the solids. All the values are equal within experimental error.

From the Table 1 we can say that the catalysts have only basic and reducing sites.No acid sites versus pyridine or cyclohexylamine[24] are present in the catalysts.This result agrees with the nature of the Ba(II) cation which does not have a strong acid character.

The number of strong basic sites,titrated by 4-methyl-2,6-diter-butylphenol(TBMPHE pKa=11.7) is greater in C-0 than in C-200 and that latter is greater than in the case of C-300.These are the sites mainly responsible for the catalytic activity of activated barium hydroxide in several organic reactions e.g:aldol condensation[17] or Wittig-Horner reaction[18];the total basicity can be titrated by benzoic acid (BA pKa=4.2) and is C-0 > C-200 > C-300.

The number of reducing sites are C-0 > C-200 > C-300.The nature of this kind of sites has been previously described[17].

The microcrystalline structure of the catalysts C-0,C-200 and C-300 has been described in a previous work[20] by discussion of thermogravimetric analysis (TGA),differential thermal analysis (DTA),IR spectra and X-ray powder diagram of the solids.A resum of the obtained results is shown in Table 2.

From the literature[22] we can deduce that in the C-0 ($Ba(OH)_2\ 8H_2O$) each Ba(II) is coodinated to $8H_2O$ and the average distance $Ba\text{-}OH^-$ and $OH^-\text{-}H_2O$ are 2.7 and 3.5 Å.,respectively.

The structure of the most active catalyst C-200 (Table 3),is shown in Figure 1.The β-$Ba(OH)_2$[25] is in the bulk of the solid.The $Ba(OH)_2\ H_2O$[26] is on the solid surface.So it will be the responsible of the catalytic activity.The average distances $Ba\text{-}OH^-$ and $H_2O\text{-}OH^-$ in $Ba(OH)_2\ H_2O$ are 2.6 and 3.89 Å,respectively.

C-300 has α-$Ba(OH)_2$ in the bulk and a small amount of $Ba(OH)_2\ H_2O$ on the surface[20].

The strong basic sites without steric hindrance of the solids titrated by TBMPHE have been related to the OH^- of the solid surface whose negative charge is not completely compensated by the positive ions from the lattice.The basic sites in the case of $Ba(OH)_2\ H_2O$ (the main component of C-200 and the secondary one in C-300),have been related to the external OH^- of the cube (Figure 1).

Table 2

Cell lattice of catalysts C-0,C-200 and C-300

C-0 catalyst

Empirical formula $Ba(OH)_2 .8H_2O$
Monoclinic structure
a_0=9.35 Å
b_0=9.38 Å $\alpha = \gamma = 90^{\circ}$ $\beta = 98.96^{\circ}$
c_0=11.87 Å

C-200 catalyst

Empirical formula $Ba(OH)_2$ 0.8 H_2O
Mixture of $Ba(OH)_2$ H_2O (main product)[a] and β-$Ba(OH)_2$ (secondary one)

$Ba(OH)_2$ H_2O orthorhombic structure[21]	β $Ba(OH)_2$ monoclinic structure
a_0=6.366 Å	a_0=9.40 Å
b_0=6.955 Å	b_0=6.79 Å $\alpha = \gamma = 90^{\circ}$ $\beta = 97.6^{\circ}$
c_0=3.890 Å	c_0=3.95 Å

C-300 catalyst

Empirical formula $Ba(OH)_2$ 0.39H_2O
Mixture of α-$Ba(OH)_2$ (main product)[b] and $Ba(OH)_2$ H_2O (secondary one)
α-$Ba(OH)_2$ orthorhombic structure
a_0=11.03 Å
b_0=16.56 Å
c_0= 7.16 Å

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[a] $Ba(OH)_2$ H_2O is produced by hydration of β-$Ba(OH)_2$[17,19] by the water in the air.Therefore the monohydrate is on the surface and the β-$Ba(OH)_2$ in the bulk.

[b] $Ba(OH)_2.H_2O$ is slowly produced by the hydration of α-$Ba(OH)_2$[17,23]

Catalytic activity

Some results obtained in the Michael addition of active methylene compounds ($CH_2R^1R^2$) to chalcone,**2**,are shown in Table 3[31].We can observe that - the obtained yields with C-200 are greater than the described in the literature and in very mild conditions.

When the three catalysts are compared in the test reaction (Michael addition of **1**), we can say that the most active catalyst is C-200.Similar affirmations can be made when C-200 and C-300 are used as catalysts in other cases (Table 3).

This fact cannot be related to the surface area because the values are similar in all cases (Table 1).

The catalytic activity of C-200 versus C-300 could be explained by the greater amount of strong basic sites without steric hindrance (titrated by TBMPHE),in C-200 than in C-300.These sites have very little steric hindrance because they are titrated by the bulky TBMPHE molecule.So,the bulky molecules **1** and **2** could react on this catalytic site because the steric hindrance cannot avoid the reaction.On

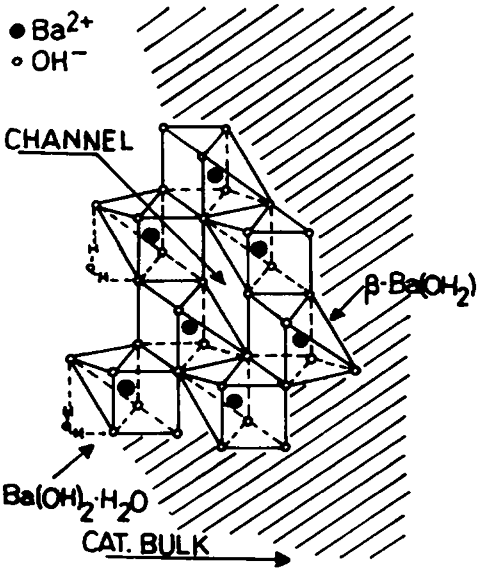
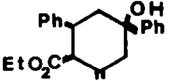
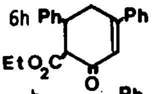
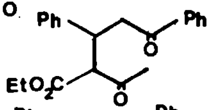
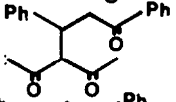
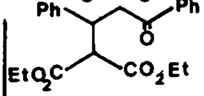


Figure 1.-Structure of C-200 catalyst

Table 3

Michael addition of active methylene compounds to chalcone,catalyzed by several barium hydroxide catalysts.Ph-CH=CH-CO-Ph + CH$_2$R^{1}R^2

Catalyst	R^1	R^2	Reaction conditions[a]	Product	Yiel (% molar) found	reported	m.p.(°C) found	lit.
C-200	CH$_3$CO	CO$_2$Et	r.T. 10h.		95	40-76[27]	162-4	162[27]
C-300	CH$_3$CO	CO$_2$Et	r.T. 10h.		65	"	"	"
C-200	CH$_3$CO	CO$_2$Et	reflux 6h		80	50-70[27]	111-2	114[27]
C-200	CH$_3$CO	CO$_2$Et	r.T. 10h.[b]		90	60-80[28]	120-1	121[28]
C-300	CH$_3$CO	CO$_2$Et	r.T. 10h.		60	"	"	"
C-200	CH$_3$CO	CO-CH$_3$	r.T. 6h		98	72[29]	145-6	146[28]
C-200	CO$_2$Et	CO$_2$Et	r.T. 8h		95	65-86[30]	65-7	67[30]
C-0	CO$_2$Et	CO$_2$Et	r.T 8h[c]		80	"	"	"
C-300	CO$_2$Et	CO$_2$Et	r.T. 8h.		52	"	"	"

[a] moles 1=moles 2=25mmol. 50mg. cat.C-200 or C-300

[b] using 5mg. of C-200

[c] using 500mg C-0

Table 4

Selective poisoning experiments of active sites in barium hydroxide catalysts in the Michael addition of 1 to 2. T=25°C,t.react.=2h;0.2g.cat.;solvent EtOH(96%),25mmol of 1 and 2.

Entry	Catalyst	Kind of active site (poisoning agent)	number of active site(meq/g.cat)	amount of adsorbed poison(meq/g.cat.)	Yield (%mol)[a]
1	C-200	-	-	-	95
2	C-200	reducing (DNB)	$(3.5 \pm 0.3)10^{-2}$	$(3.8 \pm 0.3)10^{-2}$	58
3	C-200	basic(TBMPHE)	$(6.3 \pm 0.2)10^{-3}$	$(6.7 \pm 0.3)10^{-3}$	5
4	C-300	-	-	-	52
5	C-300	reducing(DNB)	$(7.0 \pm 0.7)10^{-4}$	$(7.0 \pm 0.7)10^{-4}$	2
6	C-300	basic(TBMPHE)	$(2.2 \pm 0.2)10^{-3}$	$(2.8 \pm 0.3)10^{-3}$	5
7	C-0	-	-	-	80[b]
8	C-0	reducing(DNB)	$(5.5 \pm 0.6)10^{-2}$	$(5.2 \pm 0.5)10^{-2}$	0
9	C-0	basic(TBMPHE)	$(2.6 \pm 0.3)10^{-2}$	$(2.4 \pm 0.3)10^{-2}$	0

[a] Error ± 5%

[b] 0.5g. of C-0 catalyst versus o.2g in the case of C-200 and C-300

the other hand the pKa $\geq$11.7 of these sites is similar to the pKa of 1 (pKa=12.7),so the basicity of these sites would be valid to carry out the reaction.This affirmation agrees with the selective poisoning data (Table 4,entries 3 and 6),because the poisoning of this kind of site leads to null conversions.

The commercial barium hydroxide,C-0,is less active than the C-200 because a lower yield is obtained with 0.5g. versus 0.2g. in the case of C-200 (entry 7 versus 1,Table 4).

As in the other cases,the selective poisoning of the strong basic sites of C-0 by TBMPHE carries to zero conversions.So,we can say that the process seems to be initiated by the formation of a carbanion from 1 (pKa=12.7) on the strong basic sites without steric hindrance (titrated by TBMPHE).The analysis of the adsorbed species by IR confirm this affirmation (see below).

The role of reducing sites (titrated by DNB) is different.In the case of C-200 there is a small reduction in the yield when these sites are poisonned (entry 2 versus 1,Table 4).So,we can say that these active sites are not the main responsible of the catalytic activity in this reaction.They must be pure reducing sites (one-electron donors).Therefore the strong basic sites acting in the process are not reducing ones.They must be OH^-.These OH^- are,probably,the appical OH^- of the surfacial cube of $Ba(OH)_2$ H_2O (Figure 1).

When the reducing sites of C-300 and C-0 are poisoned,null conversions are obtained.This can be explained because in these catalysts the reducing sites are basic and reducing sites.

Both kinds of active sites have been described by Tanabe et al. for other basic solids[32,33]. The one electron donor sites would be produced by two neighbouring microcrystals and are more abundant in solids with small cell lattices than in solids with large ones.So,C-200 (practically $Ba(OH)_2$ H_2O) with smaller cell lattices thanthe C-300 (practically α-$Ba(OH)_2$) and C-0 ($Ba(OH)_2$ $8H_2O$) will practically have one-electron donor sites (no basic ones).So,the DNB poisoning cannot avoid the basic catalysis.The reducing-basic sites are $O^=$ [32,33],produced by dislocation of the cell lattice and they are abundant in solids with large cell lattices like C-0 and C-300.This fact could explain why the DNB poisons the catalysts in the Michael addition of 1 to 2 in the case of C-0 and C-300 but no in the case of C-200.

3.-Detection of adsorbed species on solids

The structure of the adsorbed species from 1 on solids (C-0,C-200 and C-300) were studied by IR spectrum of the solid after being in contact (at the reaction conditions) with 1.The PECDS program has been used by the accumulation and manipulation of the IR spectra.

When the ethanolic solution of 1 and the solid catalyst are put together in reaction conditions for some minutes (see experimental), and the mixture is filtered,no IR bands different from 1 ones were observed in the liquid in any case.

Nevertheless,when the IR spectra of difference of solids are recorded,some IR absorptions related to adsorbed species more conjugated than 1 are observed.These bands are:

1735 cm^{-1} -$\underline{CO}$-OEt (slightly conjugated)....... 1740 cm^{-1} for 1

1600-1550 cm^{-1} broad band with two maxims

1580 cm^{-1} and 1550 cm^{-1} related to $C\overset{\cdots}{-}O$ B_{1u} (1578 cm^{-1})[34] and $C\overset{\cdots}{-}C\overset{\cdots}{-}C$ B_{2u} (1527 cm^{-1}) [34] vibrations

1390 cm^{-1} and 1290 cm^{-1} (weak).They can be related to $C\overset{\cdots}{-}O$ B_{2u} (1397 cm^{-1}) [34] and $C\overset{\cdots}{-}C\overset{\cdots}{-}C$ B_{1u} (1281 cm^{-1})[34] vibrations

Therefore we can postulate 3 as the structure for the carbanion from 1 ,adsorbed on the cube of $Ba(OH)_2$ H_2O.

Similar IR spectra of difference were recorded for the adsorbed species for C-0 and C-300. So, similar adsorbed species are produced in all catalysts. This can be explained because the process takes place in the same active sites (titrated by TBMPHE).These sites would have a distance OH^--H_2O =3.9 Å,similar to the distance of the enolate ion ,3, and related to the $Ba(OH)_2$ H_2O structure. This distance is present too in $Ba(OH)_2$ $8H_2O$. So,we could say that the structure of the active site is:

a strong basic site(the OH^- ,pKa$\geq$11.7)

a water molecule at 3.9 Å.

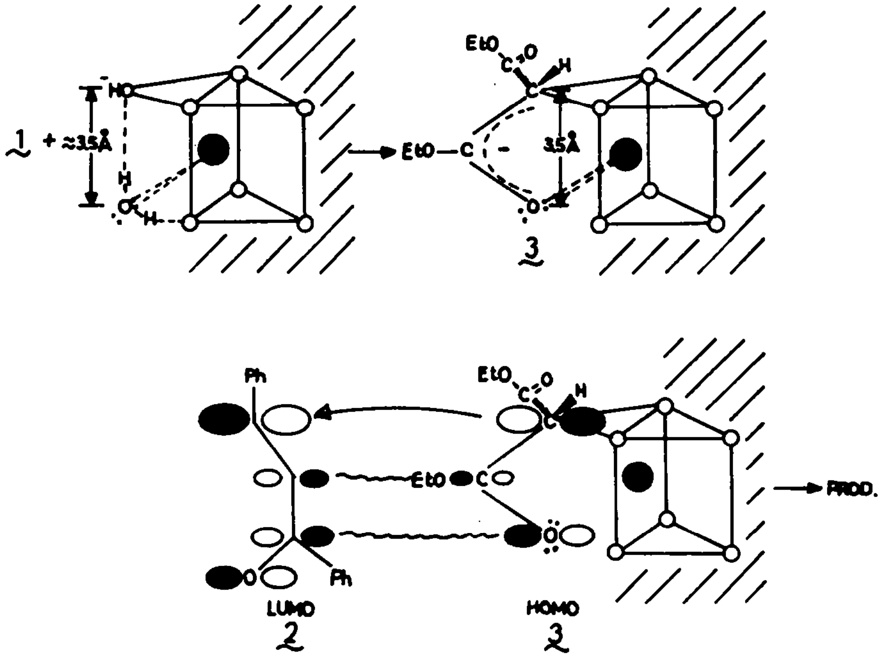
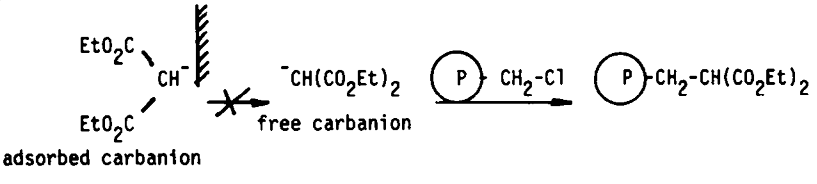


Figure 2.-Proposed mechanism for interfacial solid-liquid Michael addition of 1 to 2 catalyzed by C-200

This idea about the active site of the solid is similar to the commonly used for the receptor in Medical Chemistry.

On the other hand,the chalcone is not adsorbed in any case.So,a mechanism lika that proposed in Figure 2 could be postulated for the process,where the adsorbed carbanion reacts with the chalcone from the liquid phase.

This mechanism is supported by the fact that the carbanion from 1 is not trapped by Merrifield resin (-CH_2Cl 1meq/g),because the ester group band (CO-OEt 1740 cm^{-1}) is not observed in the polymer when the resin and the mixture of the catalyst and the ethanolic solution of 1 are put togheter for 24h.



Therefore,we can say that the carbanion remains adsorbed on the solid surface and the process is an interfacial solid-liquid mechanism (Figure 2).This behaviour is similar to that described for other organic reactions catalyzed in interfacial solid-liquid conditions by these solids e.g:aldol condensation[17],Wittig-Horner[18] etc.

EXPERIMENTAL

Catalysts

The C-200 and C-300 catalysts have been obtained by a method described previously[17].

The C-0 catalyst is a commercial $Ba(OH)_2$ $8H_2O$ (Probus S.A)

The X-ray powder diagram have been recorded in a Philips PW 1130 (35kv,35mA) using CoK (λ =1.790260 Å).The experimental conditions were $15^\circ < 2\theta < 42^\circ$;1º/min.

The nature and amounts of active sites of catalysts were determined by the method described by Sinisterra et al.[24] consisting in the titration of active sites in the solids which have very low surface area and high amount of water.

Michael addition

The Michael addition synthetic method has been described previously[20].The amount of $CH_2R^1R^2$ and **2** the reaction time are described in Table 3.All the products were from Merck p.a.

Selective poisoning experiments

The selective poisoning experiments of the catalysts have been performed using dry cyclohexanic solution of 1,3-dinitrobenzene (DNB) ($9.52\ 10^{-3}$ M) and 4-methyl-2,6-diter-butylphenol (TBMPHE) ($3.67\ 10^{-2}$ M) to poison the reducing and the strong basic sites.

0.2g. of solid are mixed with the poisoning solution for 24h. The mililitres of poisoning solution were calculated in order for the mols of poison in the solution to be five times greater than the number of active sites to be titrated. In these experimental conditions we have shown that all the poisonable sites are poisoned[20,24].

Then the mixture is filtered and washed with 2x5mL of dry cyclohexane Merck in order to eliminate the physisorbed poison. Then,the poisoned solid is added to an ethanolic solution of **1** (25mmol.) and **2** (25mmol.) and stirred during the reaction time (Table 3). Then,the barium hydroxide is destroyed by HCl 1M and the Michael adduct is extracted by 3x10mL of diethylic ether.

The reaction yield was determined by HPLC using a Perkin-Elmer chromatograph serie 2. $MeOH/H_2O$ 70/30(v/v) as the eluent.1200psi of pressure.C_8 column.

IR spectra of adsorbed species

The IR spectra of adsorbed species were recorded by a Perkin-Elmer 599B with a data Station 3600. The PECDS program was used by the accumulation and differenciation of spectra.

The experimental procedure was:

0.2g. of catalyst were added to an ethanolic solution of the product (**1** or **2**) in the reactions conditions. The mixture was stirred for 5min. to give rise the adsorption process and to avoid the decomposition of the adsorbed species produced on the solid. Then,the mixture was filtered and washed with 2x5mL of EtOH (99.8% Merck) to eliminate the physisorbed product and the IR spectrum of the solid was recorded.

Trapping experiments with Merrifield Resin.

In order to detrmine if the carbanion produced from 1,detected by IR, left the solid surface, Merrifield resin Ega-Chemie was used. No $Ph-CH_2-Cl$ was used as trapping agent because it reacts with the basic solids giving $Ph-CH_2-OH$[35].

The experimental procedure was:

25mmol. of **1**,25 mL of EtOH(96%) and 0.2g. Merrifield resin (1meq Cl/g. resin) were mixed and stirred for 48h. (an amount twice as great as the reaction time).Then,the mixture was filtered and the solid washed with 2x10mL of diethylic ether.The solid was dried at vacuum (100ºC) and the IR spectrum recorded .In any case,the 1740 cm^{-1} absorption (CO-OEt) from 1 was detected.

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