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$Ba(OH)_2$ AS CATALYST IN ORGANIC REACTIONS - PART XIX- STRUCTURE-CATALYTIC ACTIVITY RELATIONSHIP IN THE Ad_N OF SEVERAL YLIDS TO CH=O GROUP, CATALYZED BY ACTIVATED BARIUM HYDROXIDE CATALYST

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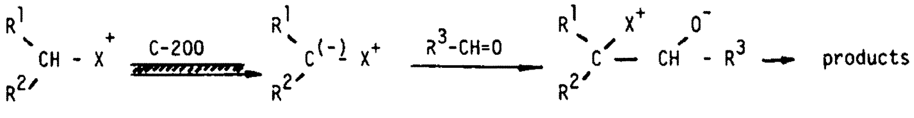
ABSTRACT.- The reactivity of several products $R^1R^2CH\text{-}X^+$, 1, (X=N,P,S), which can produce ylids by reaction with bases, has been tested using the activated barium hydroxide catalysts, C-200. Wittig-Horner, Wittig, Corey-Chaykovsky and Kröhnke type reactions have been analyzed. The pKa of 1, and the structure of active sites control the process. When 1 has a strong acid character, the process takes place -dissolving the solid- in homogeneous phase. When 1, has pKa values < 11, the process takes place in the strong basis sites of the solid (pKa > 11.7), that control the reaction mechanism and the reactivity of adsorbed ylids.

The influence of thereaction intermediates structure in the regio and stereoselectivity is well known by organic chemists[1,2]. When the reaction is carried out in interfacial solid-liquid conditions, the structure of the active site of the solid catalyst controls the structure of adsorbed reactive intermediates by means of their geometrical, steric and electrical properties. This fact is not well known by the organic chemists who use the interfacial solid-liquid conditions more and more, due to the high yields and selectivities obtained.

Recently, a new microcrystalline barium hydroxide catalyst, C-200, has been described. It is a very active catalyst for the carbanionic processes such as aldol condensation[3], Michael addition[4,5], Claisen-Schmidt condensation[6] etc.

In the present paper we analyse the Ad_N of several ylids, 2, to CH=O bond. 2, is generated from 1 by means of C-200 catalyst.



1 2 3

X=N,P,S

In all cases, The Ad_N processes have the same interfacial solid-liquid pathway:

1st step - adsorption of 1 on the active site

2nd step - formation of the ylid, 2, by reaction of 1 with tha active site of solid

3rd step - reaction of 2 with the adsorbed or unadsorbed aldehyde

The first reaction step is controlled by the steric and electronic characteristics of the active site. Only a molecule with an electrostatic charge distribution complementary to that of the active site, could be adsorbed unless the steric hindrance prevents this process.

The second step is determined by the pKa of the active site that will remove the acid hydrogen atom from 1.

The steric hindrance produced by the 2-NO_2 group near CH=O hinders the process, 11d (Table 1). This can be explained by the steric hindrance that impedes the adsorption of aldehyde at the active site of the solid. To avoid this steric hindrance, the conjugation must be broken. This fact would discourage the process.

When the aldehyde is aliphatic, the free spinning around the C-C bond might permit the bulky groups to be placed outside the solid surface. So, steric hindrance is not very important because very good yields are obtained in 12 and 13. The shorter reaction time necessary for ketophosphonates than for 7a could be explained by the higher pKa of 7b and 7c versus 7a that allows the later to react with weaker acid sites in the solid. The general scope of the catalytic activity of C-200 in the Wittig-Horner reaction has been already published by the workers.[15]

2.2.-Wittig reaction

The synthesis of chalcones, 14, as bulky conjugated α-enones was used as the Wittig reaction test. The results obtained are show in Table 2. Several aromatic aldehydes Ar-CH=O were used in order to analyse the influence of the substituents in the aromatic ring.

We can say that the electron-donating groups such as (4-CH_3 and 4-CH_3O-) discourage the process but the electron-withdrawing ones favour. It has been described in other carbanionic process.

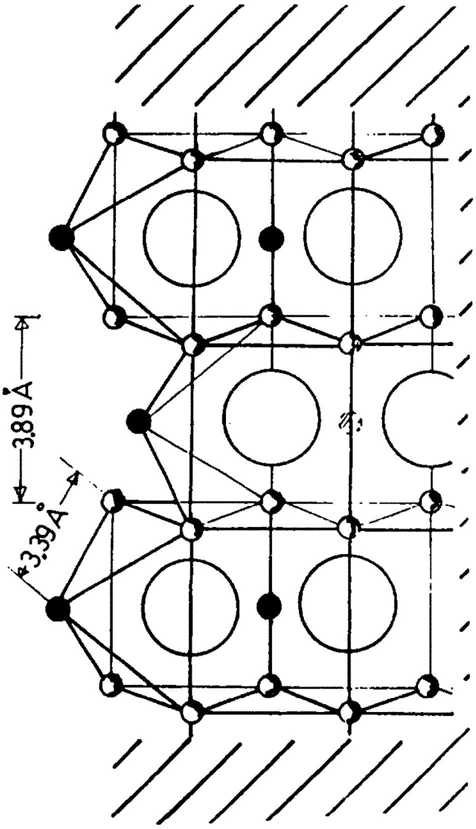


Figure 1.-Microcrystalline structure of C-200

Table 1

Synthesis of acrylates and α-enones by Wittig-Horner reaction
0.025mol of 7, 0.025mol of aldehyde, 30ml 1,4-dioxane, 0.5ml water, 2.5g. C-200, T=70ºC

R^3	Phosphonate	Product	Yield(%molar)/ react.time found	Yield(%molar)/ react.time reported
	7a	11a	100/25min.	90^{12}/60min
C_6H_5-	7a	11b	95/25min.	100^{13}/24h.
4-CH_3O-C_6H_4-	7a	11c	77/60min.	60^{14}/60min.
2-NO_2-C_6H_4-	7a	11d	93/60min.	14^{12}/60min.
3-NO_2-C_6H_4-	7a	11e	100/25min.	-^{a}
C_6H_5-CH- CH_3	7b	12b	84/10min^{b}	73 /3h(25ºC)^{c}
"	7c	12c	98/10min^{b}	91 /4h(40ºC)^{c}
C_6H_5-CH-	7b	13b	96/15min^{b}	95 /4h(40ºC)^{c}
" Bu^t	7c	13c	95/10min.^{b}	94 /3h(40ºC)^{c}

[a] Described by Sinisterra et al. using C-200 catalyst[15]

[b] These reaction was carried out mixing 7b and 7c with C-200 for 10min. Then, the aldehyde is added The mixture is stirred for the reaction time.

[c] Using the classical conditions NaH/DME.

If we compare the results obtained with those from the Wittig-Horner process, we can say that the reaction times are greater and the yields lower in in the Wittig process than in the Wittig-Horner process. On the other hand, we can say that the α-enones can be obtained more easily by

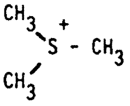
The third one is controlled by the steric factors of the cell lattice and so,by the active site.A reaction would take place if the transition state is possible inside the geometric zone around the active site that acts in the process.

If the ylid is stable, it can leave the solid surface producing the reaction in the liquid phase.Then the process could be considered a phase transfer process because the ylid is produced in the solid and reacts in the liquid phase.

The nature of the heteroatom X in 1, determines the nature of the end products.

Three different heteroatoms and therefore, three different kinds of synthetic processes were chosen.

Sulfur.-The Corey-Chaykovsky reaction using sulphonium 3,5 and sulphoxonium 4, salts for the synthesis of epoxides.[7,8]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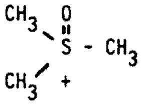
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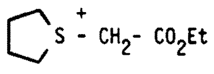
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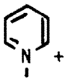
Phosphorous.- The Wittig and Wittig-Horner reaction using phosphonium salt, 6 , and phosphonates 7.[9,10]

$Ph_3\underset{+}{P} - CH_2 - COPh$

$(EtO)_2P(O) - CH_2\ R$
7a R= CO_2Et
7b R= COPh
7c R= $COBu^t$

Nitrogen.- Kröhnke type reactions[11] using pyridinium,8, quinolinium,9, and isoquinolinium,10, salts.

Ph-CO-CH_2- X^+ X^+=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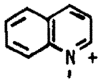
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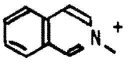
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As a result, a good deal of information concerning the mechanism of these processes -under interfacial solid-liquid conditions- are obtained from these ylids which have very different electrical and steric characteristics.

RESULTS AND DISCUSSION

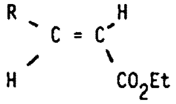
1.-Catalyst

The chemical and textural properties of the C-200 were described previously[3]. The microcrystalline structure of the solid surface is shown in Figure 1.

2.-Catalytic activity

2.1.-Wittig-Horner reaction

The catalytic activity of the C-200 in the Wittig-Horner reaction was tested in the synthesis of acrylates,11, and in the synthesis of two different bulky α-enones 12 and 13.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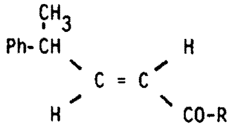
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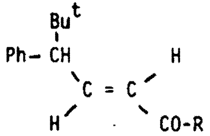
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The configuration of the olefinic compounds were E in all cases according to the ^{1}H-NMR spectra. Secondary reactions such as aldol condensation or the Cannizzaro reaction of the aldehyde were not observed in any cases. On the other hand, no isomerization of C=C was observed.

We can observe in Table 1 that electron-donating groups such as CH_3O- discourage the process while electron-withdrawing groups favour it.This is in accord with the classic Wittig-Horner mechanism where the ylid reacts with the electrophile C=O group. In all cases the obtained yields with C-200 are better than those obtained with other solid bases in similar conditions (see Table 1).

Table 2
Synthesis of chalcones by Wittig reaction
0.025mol of aldehyde, molar ratio ArCHO/6=1 and cat/6=0.5, 2.4g of C-200, T=70ºC

Ar-CH=O	Chalcone	Yield (% molar)/ reaction time	
		found	reported
$4\text{-Cl-}C_6H_4\text{-CHO}$	14a	49 / 90min.	94-8/60 min[a,16]
$4\text{-NO}_2\text{-}C_6H_4\text{-CHO}$	14b	80 / 90min.	94-7/60min.[a,16]
$3\text{-NO}_2\text{-}C_6H_4\text{-CHO}$	14c	52 / 60min.	-[b]
$4\text{-CH}_3\text{-}C_6H_4\text{-CHO}$	14d	20 / 60min.	-[b]
$4\text{-CH}_3O\text{-}C_6H_4\text{-CHO}$	14e	36 /120min.	92-5/60min.[a,16]

[a] Obtained by Claisen-Schmidt reaction at reflux of EtOH. Catalyst C-200

[b] No product obtained with C-200

the Claisen-Schmidt process than by Wittig reaction[6,16] using the same catalyst.

Potassium carbonate seems to be of more interest than C-200 in the Wittig process because high yields are obtained and low reaction times are described by the synthesis of similar steric hindrance[17].

2.3-Epoxide synthesis.

The synthesis of epoxides by Corey-Chaykovsky reaction was studied using the C-200 catalyst. The results are shown in Table 3.

Table 3
Epoxide synthesis
0.012mol of 3,4 or 5; 0.012mol of aldehyde, 2g. of C-200, 20ml of acetonitrile

Salt	Ar-CHO	Temp.reaction	t(min)	Yield(%molar)
3	furfural	reflux of CH_3CN	180	0[a]
5	" [b]	"	180	3
4	"	"	120	38
4	$4\text{-CH}_3O\text{-}C_6H_4\text{-CHO}$	"	90	5
4	$4\text{-CH}_3\text{-}C_6H_4\text{-CHO}$	"	90	0
4	$4\text{-Cl-}C_6H_4\text{-CHO}$	"	90	8
4	$3\text{-NO}_2\text{-}C_6H_4\text{-CHO}$	"	90	80
4	$4\text{-NO}_2\text{-}C_6H_4\text{-CHO}$	"	60	100

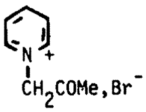
[a] No reaction was observed in other cases

[b] No reaction was observed with other aldehydes

Null or very poor yields are obtained in the case of sulphonium salts. When sulphoxonium salt is used, moderate or good yields are obtained with strong electrophilic aldehydes (furfural, 3-NO_2 and 4-NO_2-benzaldehydes) but null conversions are obtained in other cases. This fact could be explained assuming that the ylid produced on the solid is very unstable due to the low conjugation of the negative charge.

2.3-Kröhnke reaction

Several pyridinium, quinolinium and isoquinolinium salts were used in order to produce ylids with different geometrical and electrical characteristics.



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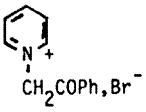

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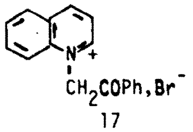

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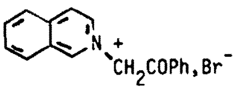

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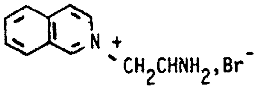

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In any cases Ad_N reaction products were isolated. Nevertheless the ylid is produced on the solid, due to the strong colours which are produced on the solid when the salt is added to C-200. On the other hand, the ylid is detected by IR. Therefore we can say that the ylid is produced on the solid but is not reactive since the coloured solid and the solutions are relatively stable in open vessel, under atmosphere.

3.-Selective poisoning experiments

In order to explain the difference in catalytic activity previously described, additional experiments were carried out.

Selective poisoning experiments of the strong basic sites (pKa 11.7) by 4-methyl-2,6-diterbutylphenol (TBMPHE) give null conversions in the case of Wittig-Horner (using 7a) and in Corey-Chaykovsky reactions which agrees with the reported pKa for 7a (pKa=12.2 in diglyme - similar to 1,4-dioxane[17,18]) and for Et_2MeS^+ (pKa=11.12)[19]. This compound would have a similar pKa of 4 and 5 (we have not found these pKas in the literature). All these values are very similar to the pKa of TBMPHE (11.7) explaining the poisoning effect observed. Therefore we can say that the strong basic sites of C-200 (pKa>11.7) are responsible for the production of ylids in these cases and therefore, also for the reaction processes.

The pKa of $Ph_3P^{(+)}CH_2COPh$, 6 is 5.6[19]. We could assume that the pKa of the ketophosphonates 7b and 7c would be similar. Then, we can explain why no poisoning is observed when the strong basic sites versus TBMPHE are poisoned. The benzoic acid, BA, (pKa 4.2) does not poison these processes. This could be explained by the total or partial dissolution of C-200 catalyst by these compounds as has been proved experimentally. Therefore ylid formation takes place by direct reaction of phosphorous compound and the OH^- from the lattice of activated barium hydroxide, C-200. The steric hindrance in all the cases of phosphorous salt makes the ylid go to the liquid phase -- where the reaction with aldehyde takes place. Probably better yields are obtained with 7b and 7c than with 6 because the ylid from 6 is more unstable than those from 7b and 7c. Therefore they can react quickly with the water in the interface solid-liquid again giving 6 and diminishing the yield.

4.-Structure of adsorbed ylids

In order to supply data to explain the catalytic activity of C-200, the structure of adsorbed ylids on C-200 was determined. Previously we have reported that aldehydes are adsorbed on the catalyst by $\pi^2 C{=}O \rightarrow 5d^0$ Ba(II) bond[20].

4.1-Wittig-Horner ylids.

When the adsorption of 7b and 7c on C-200 are carried out, the solid is dissolved. Therefore, we can say that these processes take place in a homogenous phase. Similar results were obtained in the Michael addition of acetylacetone (pKa=9) to chalcone. This strong acid dissolves the solid giving barium salts that we have characterized[24]. This fact confirms that the processes with strong acids take place in the homogeneous phase.

To the contrary, the adsorbed ylid from 7a can be detected by IR spectroscopy (Table 4). In this case we can say that it is not the CO-OEt bond that is present in the adsorbed species but a $1670cm^{-1}$ band that can be related to $C \cdots O_5$ bond. This absorption is similar to $1620cm^{-1}$ described by Seno et al.[21] for CO of $Ph_3P{=}CH{-}CO_2Me$. Two bands at 1570 and $1384cm^{-1}$ could be related to $C_1 \cdots C_2$ vibrations and the $1194cm^{-1}$ to the $P \cdots O_6$ according to the literature data for the Z form of ylid in the presence of K(I) or Li(I)[22]. No $P \cdots C_1$ absorption is detected.

The presence of adsorbed species of the ylid from the weak acid 7a (pKa=12.2[17]) on C-200 is similar that described for the Michael addition of diethyl malonate(pKa=12.0) to chalcone[24].

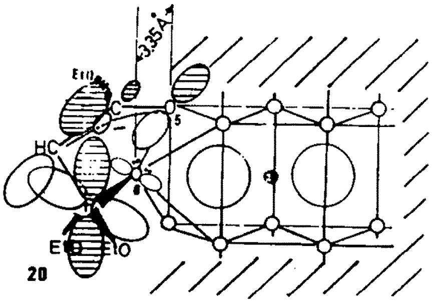

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Figure 2.- Structure of adsorbed ylid from 7a

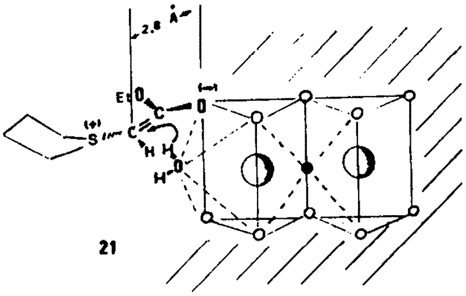

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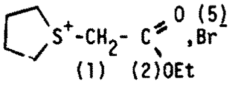
Figure 3.-Structure of adsorbed ylid from 5

Taking into account the structure of the C-200 (Figure 1) where the OH^- and H_2O are placed at 3.39Å, we can postulate a structure like 20 for the adsorbed ylid where the O_6^- is placed where the OH^- had been in the cell lattice. The $C_1 \overset{-}{=} C_2$ and $C_2 \overset{-}{=} O_5$ are not conjugated with the phosphorous because no $P \overset{-}{=} C$ bond is observed by IR. Thus the negative charge is divided between the C_1 and the O_5. The O_6 with two alone electron pairs is placed where the oxygen from the water has been in the cell lattice (Figure 2).

Table 4



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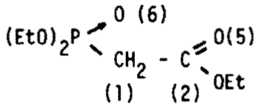

7a

Main Ir bands(cm^{-1}) of 5 and 7a and their ylids adsorbed on C-200.

	5	ylid	7a	ylid
ν $C_2=O_5$	1740	-	1740	-
ν $C_2 \overset{-}{=} O_5$	-	1640	-	1670
ν $C_1=C_2$	-	1612	-	-
ν $C_1 \overset{-}{=} C_2$	-	-	-	1570
ν $C_1 \overset{-}{=} C_2$	-	-	-	1384
ν $P \rightarrow O_6$	-	-	1275	-
	-	-	1210	-
ν $P \overset{-}{=} O_6$	-	-	-	1194

When the adsorption of 7b and 7c on C-200 are carried out, the solid is dissolved. Similar - behaviour was observed with acetylacetone (pKa=9)[24]. Therefore, it seems that acid with high pKa values produces dissolution of the C-200 giving barium complex salts that react with the Ar-CHO in the homogeneous phase (e.g:7b and 7c). In this case the process is a phase trnasfer reaction. The ylid is produced in the solid surface and goes to the liquid phase. When the ^{31}P-NMR spectra of these solutions were recorded at 32.2MHz. only a broadened singlet was observed and the ^{31}P signal appears shifted to low-field with respect to the 2-oxalkanephosphonate.

$\Delta\delta$ ^{31}P $\underset{(-)}{Ph\text{-}CO\text{-}CH}\text{-}P(O)(OEt)_2$ 13.0 ppm $\underset{(-)}{Bu^t\text{-}CO\text{-}CH}\text{-}P(O)(OEt)_2$ 14.3ppm

These ^{31}P down-field shifts are in agreement with the literature data[25] and confirm the presence of anionic species in the liquid phase.

When the acid is very weak, the ylid remains adsorbed in the solid and it is stabilized by the charge delocalization between the ylid and Ba(II) (e.g:7a). In this case the reaction only takes place when the ylid has a geometry and charge distribution similar to those of the active site (see Figure 2). Se wee are confronted by a reaction in the interface solid-liquid, sensitive to the structure of the solid.

4.2-Wittig ylid

When the adsorption of $Ph_3P^+\text{-}CH_2COPh$ (pKa=5.6) is attempted, this ketophosphonium compound dissolves the C-200 catalyst as do the other ketophosphonates,7b and 7c. Furthermore the solution turns yellow but this colour is unstable. Unfortunately, the presence of the solvent (1,4-dioxane and water) prevented the detection of the possible barium complex by Ir spectroscopy.

Therefore, the high pKa value of phosphonium salt is mainly responsible for the occurrence of the process in the homogeneous phase.

4.3-Sulfur ylids

The very low yields obtained with 5 can be explained by the structure of the adsorbed ylid. From the data in Table 4 we can deduce that the C=O bond is not present in the adsorbed species. Two absorptions at 1640 and 1612cm^{-1} are present in the adsorbed species. The first band must be assigned to the stretching of a C=O which is so relaxed that is practically C-O. The 1612cm^{-1} absorption is a quasi C=C bond. Therefore we can say that the adsorbed specie could be described by 21 (Figure 3).

No carbanionic character is present in the CH and no reaction with C=O is possible according to our results.

In the case of the sulphoxonium salt, instead of observing the S=O absorption in the adsorbed species, there is a $850cm^{-1}$ that could be related to S-Ost. according to the literature[26]. Unfortunately the presence of S=C bond (absorption $1275-1030cm^{-1}$,[26]) cannot be observed due to the presence of a large band of water in the solid $1300-890cm^{-1}$.

Therefore we could postulate, at a qualitative level, a structure like 22 (Figure 4), for the adsorbed species. In this case the adsorbed ylid replaces the water molecule of $Ba(OH)_2.H_2O$ and the OH^- by the oxygen of sulphoxide group and the CH_2^-. So, the positive sulphur atom is outside the Ba(II) zone and does not unstabilize the ylid.

Therefore we have another example of weak acid, the $(CH_3)_3S^+(O)$ that gives a reaction on the solid surface due to the fact that the OH^- and the water molecule from the cell lattice are at the similar distance than the oxygen and the CH_2 from the sulphoxonium ylid (Figure 4).

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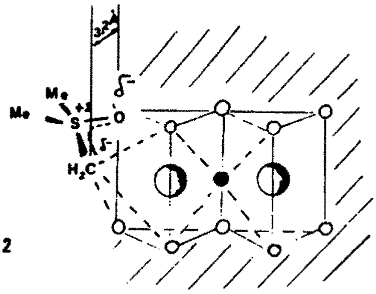


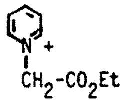
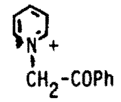
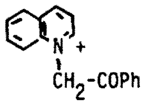
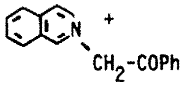
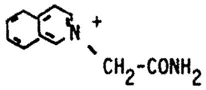
Figure 4 Structure of adsorbed ylid from the sulphoxonium salt.

4.4.-Kröhnke reaction

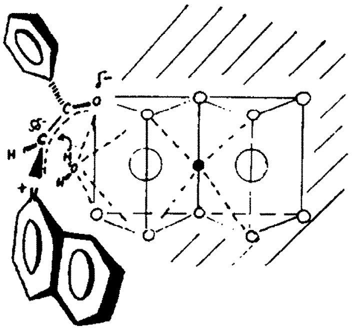
When the pyridinium, quinolinium and isoquinolinium salts are adsorbed on C-200, a strong colour results (red,orange,violet etc.), that can only be explained if we assume the formation of a charged species (the ylid). Then, the liquid becomes the same colour as the solid allowing to say that the ylid is produced on the solid surface of solid and is stable because it goes to the liquid phase. The colour of the liquid phase remains for several minutes.

The main Ir bands of the salts and their ylids are shown in Table 5. In all cases the aromatic zone is disturbed. This can be explained by the interaction of the heterocyclic ring with the charged surface. On the other hand, in all cases two characteristic bands are present near 1320 and $1370cm^{-1}$ that could be related to the C=C=N bond by its similarity to the C=C=C ($1300-1280cm^{-1}$) and C=C($1384cm^{-1}$)[22].

Table 5
Characteristics bands of pyridinium, quinolinium and isoquinolinium salts and their ylids.

azinium salts	ν (cm^{-1})	ylid ν (cm^{-1})
	-C=O 1746	- N=C=C 1317 C C 1384
	-C=O 1684	- N=C=C 1317 C=C 1374
	-C=O 1694	- N=C=C 1316 C=C 1372
	-C=O 1687	- N=C=C 1316 C=C 1372
	-C=O 1693	- N=C=C 1320 C=C 1372

Therefore a structure like 23 (Figure 5), could be pictured for nitrogen ylids. In this case the water molecule from the cell lattice is not replaced due to the presence of the N^+ as in the case of 21.



23

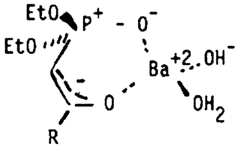
Figure 5.-Structure of adsorbed ylid from quinolinium salt

The delocalization of the negative charge by the heterocyclic ring increases the stability of 23 versus21 and explains why this ylid can go to the liquid phase where has a long life.

5.-catalytic activity versus structure of the solid

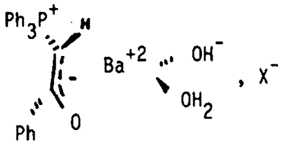
From the results of this paper we can say that there are two different kinds of mechanisms in the processes studied.

Phase transfer like mechanism.-This process takes place with high acid molecules such as 6,7b,7c and with heterocyclic salts. In all cases the catalyst is dissolved - total or partially- and the complex salts such as that described for acetylacetone could be postulated[26]. The presence of the phosphorous ylids in the liquid phase has been detected by ^{31}P-NMR.

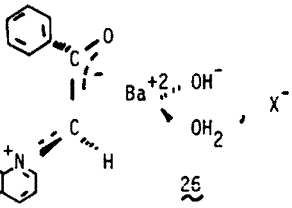


R ≠ CO_2Et

24



25



26

In these cases the reactions are not sensitive to the structure and the selective poisoning of the active sites of the solid does not produces null conversions. These reactions take place in the homogeneous phase and the yield is related-qualitatively- to the steric hindrance around the CH^-.

$$X_{24} \gg X_{25} \gg X_{26}$$

Interfacial solid-liquid mechanism

The mechanism takes place with weak acids such as 7a, 4 and 5. The process takes place in the strong basic sites titrated by TBMPHE (pKa > 11.7).

The structure of active sites controls the process because it is necessary to have an adsorbed species with two bonds to the solid, with a negative charge and an oxygen at 3.39A. This is the distance between the OH^- and the water molecule in the cell lattice of barium hydroxide monohydrate.

20 is more stable and reacts better than 22 where the small delocalization of the negative charge makes the ylid hard and unstable. Therefore, epoxides are only obtained with reactive aldehydes (see Table 3).

In 21 there is a positive charge in the sulphur atom that is repulsed by Ba(II). On the other hand the distance $O_5 - C_2 - \dot{C}_1$ is not 3.39Å and so, 21 is very unstable and reacts to the unremoved water molecule, giving very poor yields in epoxide.

The sulphonium ylid from trimethylsulphonium iodide,3, has no steric and electric conditions to be adsorbed on the cell lattice, so that no reaction is observed.

Then we can say that the basic solids do not catalyse all the possible carbanionic processes. The pKa of the acid organic compound and the cell lattice of the solid control the process and the mechanism.

EXPERIMENTAL

Catalyst

The C-200 catalyst has been obtained by a method described previously[28]. The surface area was determined by a Sorptomatic Carlo-Erba.

The nature and amount of catalyst active sites were determined according to the method described previously[29]. Benzoic acid,BA (pKa=4.2) and 4-methyl-2,6-diterbutylphenol,TBMPHE, - - - (pKa=11.7) were used to titrate the basic sites.

Synthetic procedure

i)Wittig-Horner reaction

a)Synthesis of acrylates.- The aldehyde (0.025mol), triethyl phosphonoacetate,7a,(0.025mol), 1,4-dioxane (30ml),C-200 catalysts (2.5g) and water (0.5ml) are successively introduced into a 100ml flask fitted with mechanicla stirrer, a thermometer and a reflux condenser. The reaction mixture is filtered and purified by chromatography on a short column of silica gel Merck 40, using hexane/diethyl ether (1/1,v/v) as the eluant. The solvent is evaporated and the product recrystallized or distilled.

The reaction yiels as well the purities of the end products were determined by G.L.C. (Intermat 120DFL) using a colum 3m x 1/8in. 5%OV 101 on Chromosorb W-HMDS 80-60. Carrier gas N_2=50cc/min. Initial T=140ºC, end T=260ºC[15].

b)Synthesis of α-enones.-The synthesis was 0.25g of C-200; 2.5mmol of 7b or 7c and 6ml of 1,4-dioxane were mixed and stirred at 70ºC for 10min. to produce the ylid. The formation of the ylid can be visually observed because the reaction mixture turns orange from 7b and whitish from 7c. Then, 2.5mmol of the aldehyde in 2ml of 1,4-dioxane with 0.05ml of water were added to the reaction mixture. The HCl 1M was added till acidic pH to destroy the basic solid.

The acyclic α-enones were extracted from the reaction mixture by diethyl ether (3x20ml). The reaction yield was determined by GLC (10% BDS on Chromosorb W-AW). The column temperature and the carrier gas flow (N_2) were 150ºC and 50cc/min for 7b and 130ºC and 50cc/min for 7c.

ii)Wittig reaction

25mmol of aldehyde; 10.4(25mmol) of 6, 2.4g of C-200,30ml of 1,4-dioxane and 0.5ml of water are mixed and heated at 76ºC for the legth of the reaction time. The reaction mixture was analyzed by HPLC using a HPLC chromatograph Perkin-Elmer Series 2 with a UV-visible detector (λ=254nm) and 5μ C_{18} column. $MeOH/H_2O$=80/20(v/v) as eluant and a flux=1.0ml/mim.

ii)Corey-Chaykovsky reaction

a)Synthesis of ethyl 2-tetrahydrotiophenium)-acetate bromide,5.

The synthesis of 5 is carried out dissolving 250ml (2.97mol) of tetrahydrotiophene in 100ml of dry acetone. Then, 318ml of $ClCH_2CO_2Et$(2.97 mol) were added, slowly. The mixture is cooled in a ice-water bath during the addition. Then, the mixture is heated at reflux of acetone for 24h.

The sulphonium salt is filtered and washed with dry acetone.

b)Synthesis of epoxides.- 2.65g (12mmol) of trimethylsulphoxonium iodide (Ega-Chemie) and 2.0g of C-200 catalyst are mixed in 20ml of acetonitrile (Ferosa S.A.) with 0.005mol of water. The mixture is heated at reflux of acetonitrile and then, 12mmol of aldehyde in 1ml of acetonitrile is added slowly. During the aldehyde addition, the mixture turns orange.

Then, the products are analyzed by HPLC using a 5μ C_{18} column and $MeOH/H_2O$ 80/20(v/v) as eluant. Flux= 1.2ml/min.

iv)Kröhnke reaction.

a)Synthesis of pyridinium, quinolinium and isoquinolinium salts.

These compounds were obtained by reaction at room temperature of $ClCH_2CO_2Et$, $ClCH_2COPh$ and $BrCH_2CONH_2$ with pyridine, quinoline and isoquinoline using dry acetone as the solvent.

b)The Ad_N reaction was carried out by a method similar to that described by Katrizky et al.[11].

v)The selective poisoning experiments

Benzoic acid (BA) and 4-methyl-2,6-diterbutylphenol (TBMPHE) were used to poison the basic sites. 1,3-dinitrobenzene (DNB) to poison the reducing sites and pyridine (Py) for the acid ones. The method has been described previously[29].

vi)Ir spectra of adsorbed species.

The adsorption experiments were carried out under experimental conditions equal to the those described in the experimental procedure. The adsorption time was reduced to 1/3 the reaction time in order to avoid the decomposition of the adsorbed carbanion.

Then, the solid was filtered and washed with clean solvent to eliminate physisorbed molecules of reagent and the solid was dried at vacuum. The Ir spectra of these solids were recorded on an IR-Perkin-Elmer apectrometer 599B, using a data Station Perkin-Elmer 3600 for accumulation of spectra (PECDS program).

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