Aluminophosphates oxynitrides as base catalysts for the production of dicyanomethylene derivative dyes

M.J. Climent, A. Corma*, R. Guil-Lopez and S. Iborra

Instituto de Tecnología Química (UPV-CSIC), Universidad Politécnica de Valencia, Avda. los Naranjos s/n,
46022 Valencia, Spain
E-mail: acorma@itq.upv.es

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The two-step synthesis of dicyanomethylene derivative dyes has been performed using as base catalysts MgO, calcined hydrotalcites and ALPON. These solids catalyse with good conversions and selectivities the Knoevenagel reaction step, but only ALPON catalysts are able to catalyse efficiently the two reaction steps, as well as the global reaction in a "one-pot" system.

KEY WORDS: ALPON; base catalysts; dicyanomethylene derivative dyes; Knoevenagel; MgO; calcined hydrotalcites

1. Introduction

Knoevenagel condensation is a reaction in organic chemistry that has numerous applications in the synthesis of fine chemicals, since it allows preparation of alkenes from molecules containing carbonyl groups. These reactions are classically catalysed by bases or by a combination of acid–base pairs in liquid phase systems.

Malononitrile is a versatile reactant which contains a reactive methylene group that can be condensed with carbonyl compounds through the Knoevenagel condensation yielding dicyanomethylene groups ($(CN)_2C{=}$). These groups are very powerful electron acceptors, and therefore malononitrile appears as a suitable building block for numerous methyne dyes. Dicyanomethylene derivative dyes have a variety of applications, for instance as textile dyes [1] and in sensitising photopolymerisation in imaging systems [2]. Moreover some of them, because of their light absorption properties in the near-IR region (*i.e.*, beyond 700 nm) [3], have found application in dye lasers [4], optical recording [5], and other electro-optical applications.

The aim of this work is the preparation of 1,1-dicyanomethylenebutadiene derivatives (**5**) (scheme 1) by Knoevenagel-type condensation using well defined solid basic catalysts. 1,1-dicyanomethylenebutadiene derivatives have been described as disperse dyes [6] with interesting non-linear optical properties [7,8].

The formation of dicyanomethylenebutadiene derivatives involves two reaction steps (scheme 1). The first one is the Knoevenagel condensation of acetophenone (**1**) and malononitrile (**2**) to give the corresponding α-methylbenzylidenemalononitrile (**3**) plus water (scheme 1(A)). Subsequent condensation of (**3**) with benzaldehyde (**4**) gives the 1,1-dicyano-1,3-butadiene dye (**5**) (scheme 1(B)).

The reported method of choice for carrying out both condensation steps consists in refluxing the corresponding reactants in benzene, removing the water formed by a Dean–Stark system and using a mixture of ammonium acetate and glacial acetic acid as catalyst [8,9].

With the aim of developing an environmentally more friendly process, we have considered here the possibility of using solid bases for catalysing the two-step process. It has been reported that it is possible to prepare solid bases within a wide range of basic strengths, in order to select the most appropriate basicity to catalyse selectively the desired reaction. In this sense, solid base catalysts such as alkali-exchanged zeolites [10], sepiolites [11], organic resins [12], mixed magnesium aluminium oxides derived from hydrotalcites [13–15], and more recently, aluminophosphates oxinitrides (ALPON) [16] which can cover a wide range of the basic strengths have been used at the laboratory scale to catalyse different organic reactions.

In the present work we have studied the possibilities of different solid base catalysts with different base strengths for the preparation of dyes based on the 1,1-dicyanobutadiene structure. The influence of chemical composition of the catalysts on the two-step synthesis as well as in the "one-pot" synthesis has been studied.

2. Experimental

2.1. Materials

ALPONs were prepared starting from an aluminium phosphate precursor ($AlPO_4$) with a P/Al ratio of 0.9, which was obtained following the method proposed by Kearby [17]. The nitridation procedure was performed following a previous publication [16] by flowing a stream of pure ammonia flow (150 $ml\,min^{-1}$) over the aluminophosphate pre-

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* To whom correspondence should be addressed.

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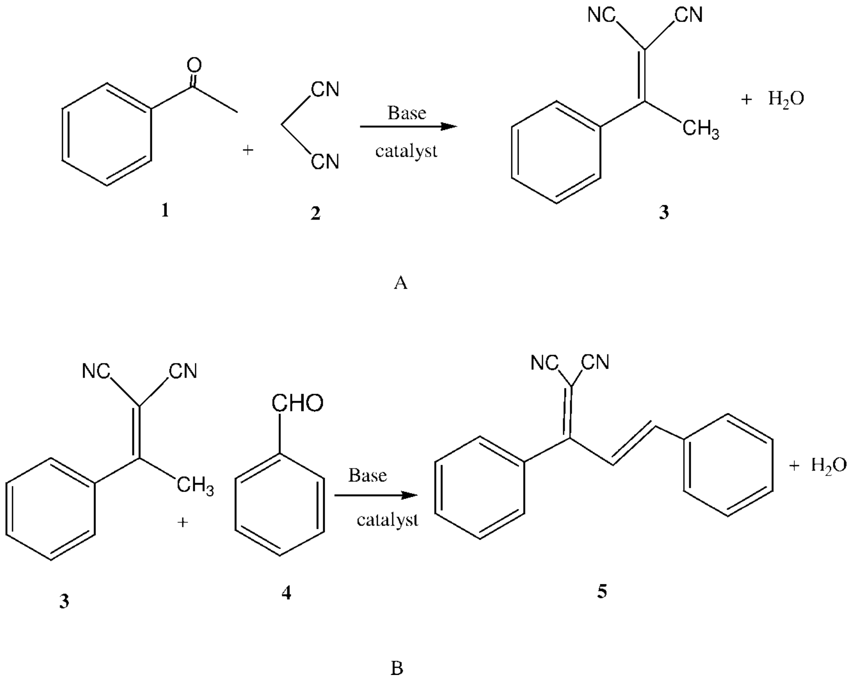


Scheme 1.

Table 1
Main characteristics of the catalysts.

Catalyst	Nitridation time[a] (h)	Nitridation temperature[a] (K)	Atomic ratio Al : P : N	N (%)	Surface[b] ($m^2 g^{-1}$)	Al/ (Al + Mg)	Crystallite size[c] (μm)
ALPON-0	–	–	–	–	208	–	–
ALPON-1	16	773	1 : 0.95 : 0.09	1.2	199	–	–
ALPON-2	16	973	1 : 0.95 : 0.42	5.1	210	–	–
ALPON-3	16	1073	1 : 0.95 : 0.70	8.3	220	–	–
ALPON-4	16	1123	1 : 0.95 : 1.17	13.7	190	–	–
MgO	–	–	–	–	200	0	–
HT-1	–	–	–	–	211	0.20	0.2–0.6
HT-2	–	–	–	–	251	0.25	0.2–0.5
HT-3	–	–	–	–	246	0.33	0.2–0.6

[a] Ammonia flow 150 ml min^{-1}.
[b] Determined by N_2 physisorption and following the BET procedure.
[c] Determined by SEM.

cursor calcined at 773 K. Temperature of nitridation was varied in order to incorporate different amounts of nitrogen. At the end of the nitridation procedure, samples were treated with a dry stream of nitrogen (99.99%). The nitridation conditions and the main characteristics of the resultant aluminophosphates oxynitrides (ALPON) are reported in table 1. Elemental analyses were carried out on the as-synthesised ALPON materials by using a CHNS analyser (Fisons EA 1108).

The preparation of the magnesium oxide was based on a modification of the method described by Putanov [18], and was directed to obtain a high surface area magnesium oxide. The MgO was obtained by calcination of a magnesium oxalate at 973 K for 3 h. The magnesium oxalate was prepared at 313 K by adding a solution of oxalic acid (2 M) to a magnesium acetate solution (2.5 M). Before calcination the magnesium oxalate was filtered, washed and dried overnight at 353 K.

Al–Mg hydrotalcites were prepared from the gel produced by mixing two solutions: solution A, containing $Mg(NO_3)_2$ and $Al(NO_3)_3$ 1.5 M in Al + Mg, with Al/(Al + Mg) atomic ratios equal to 0.20, 0.25 and 0.33, and solution B prepared by dissolving Na_2CO_3 and NaOH to achieve a Na_2CO_3 concentration equal to 1 M. The solutions were mixed at 60 ml h^{-1} addition rate for 4 h with vigorous stirring. The concentration of NaOH was adjusted to obtain pH = 13. The gels were aged at 473 K for 18 h, and then filtered and washed to pH = 7. After drying the solids at 353 K for 12 h, the hydrotalcites were calcined at 723 K in air in order to obtain Mg–Al mixed oxides [13,14]. Composition, surface areas and particle sizes of the calcined basic catalysts are presented in table 1.

Table 2
Condensation of acetophenone (**1**) and malononitrile (**2**) on different basic catalysts (5 wt%) without solvent at 373 K.

Catalyst	N (%)	Initial rate r_0 (mol h^{-1} g^{-1}) $\times 10^3$	Yield of **3**[a] (%)
ALPON-0	0	0	0
ALPON-1	1.2	8.1	10
ALPON-2	5.1	21.4	20
ALPON-3	8.3	42.8	46
ALPON-4	13.7	72.0	60
MgO	–	35.5	27
HT-2	–	30.0	22

[a] 3 h reaction time.

2.2. Reaction procedures

2.2.1. Preparation of α-methylbenzylidenemalononitrile (3)

Reactions were carried out under nitrogen atmosphere, in a flask that was fitted with a reflux condenser. The flask was immersed in a thermostated silicone oil bath and the reaction mixture was magnetically stirred. A mixture of acetophenone (**1**) (7.5 mmol) and malononitrile (**2**) (7.5 mmol) was placed in the flask. Once the mixture reached a temperature of 373 K, the desired quantity of the base catalyst was added in order to have a mixture in which the amount of catalyst is 5 wt% with respect to the weight of the reactants. MgO and hydrotalcite catalysts were reactivated before use by calcining in vacuum at 698 K. After the reaction, the mixture was dissolved in CH_2Cl_2, and the catalyst filtered and washed with dichloromethane.

Samples were periodically withdrawn from the reaction mixture by means of a filtering syringe, and the reaction products were analysed by gas chromatography (GC) (Hewlett–Packard 5890 apparatus with flame ionisation detector and using a 25 m capillary column of 5% cross-linked phenylmethylsilicone).

The reaction was also carried out in homogeneous phase following the classical method reported in [8,9]. In this case a mixture of **1** (7.5 mmol) and **2** (7.5 mmol), ammonium acetate (1.5 mmol), and 0.3 ml of glacial acetic acid were dissolved in dry benzene (50 ml). The mixture was heated in a Dean–Stark water trap for 8 h. After this, the solution was washed with water, dried with magnesium sulphate and the solvent distilled in vacuum. Yield of (**3**) was determined by GC and ^{1}H-RMN.

α-methylbenzylidenemalononitrile (3): ^{1}H-NMR: 7.78–7.50 (m, 5H, Ar$\underline{H}$), 2.65 (s, 3H, C$\underline{H}_3$). MS: 168 (M^+, 100), 153 (6), 140 (41), 128 (33), 114 (16), 103 (16), 77 (15).

2.2.2. Preparation of 1,1-dicyano-2,4-diphenyl-1,3-butadiene (5)

A solvent free mixture of **(3)** (4 mmol) and benzaldehyde (**4**) (4.4 mmol) was heated under inert atmosphere at 398 K in a batch glass stirred reactor. When the reaction temperature was stabilised, the catalyst (5 wt%) was added, following the procedure described above. MgO, HT-1, and HT-3 catalysts were reactivated before use by calcining in vacuum at 698 K.

The reaction in homogeneous phase was carried out by heating a mixture of **3** (5 mmol), benzaldehyde (6.5 mmol), ammonium acetate (1 mmol), and 0.2 ml of glacial acetic acid in benzene (50 ml) in a Dean–Stark water trap following the same procedure as described above.

trans-1,1-dicyano-2,4-diphenyl-1,3-butadiene **(5)**: ^{1}H-NMR: 7.80–7.37 (m, 11H, Ar$\underline{H}$ + C(CN)$_2$C$\underline{H}$=CH), 6.88 (d, 1H, $J = 16.0$ Hz, CH=C$\underline{H}$–Ph); MS: 256 (M^+, 60), 230 (10), 227 (15), 191 (25), 178 (43), 151 (20), 114 (25), 77 (20).

2.2.3. Preparation of 1,1-dicyano-2,4-diphenyl-1,3-butadiene (5) in one pot

A solvent free mixture of acetophenone (4 mmol) and malononitrile (4 mmol) was heated at 373 K in inert atmosphere while stirring. When the reaction temperature was stabilised, the solid catalyst (185 mg) was added. When the yield of **3** was 90% the temperature was raised up to 423 K and then benzaldehyde (9 mmol) was added.

^{1}H NMR spectra were measured in $CDCl_3$ with a 400 MHz Varian VXR-400 S instrument; chemical shifts are reported in δ (ppm) values, using TMS as internal standard. Mass spectra were obtained under electron impact using a Hewlett–Packard 5988 A spectrometer; the ratios m/z and the relative intensities (%) are reported. Isolation and purification of the products were done by conventional column chromatography on silica gel Merck 60 (0.063–0.200 mm), using dichloromethane as eluent.

3. Results and discussion

3.1. Preparation of α-methylbenzylidenemalononitrile (3)

In order to study the first step of the reaction and with the aim ofselecting the most appropriate catalysts for the preparation of α-methylbenzylidenemalononitrile (**3**), three catalysts were prepared: two catalysts with medium-strong basicities such as MgO and an aluminium magnesium mixed oxide derived from hydrotalcite (HT-2), and an aluminophosphate oxynitride with a nitrogen content of 8.3% (ALPON-3).

The condensation between acetophenone and malononitrile was carried out in absence of solvent, and the initial rates calculated dividing the conversion ($x \leqslant 15\%$) by the time of reaction, as well as the yields of **3** obtained after 3 h of reaction time are given in table 2.

According to the reaction mechanism accepted when using a conventional homogeneous base catalyst, the reaction starts with the abstraction of a proton of the methylene group by the base with the formation of the corresponding carbanion. The formed carbanion attacks the carbonyl group of the aldehyde or ketone giving the corresponding intermediate alcohol of the condensed product. In a last step, water is removed and the olefin formed. This reaction mechanism seems to apply also when using solid bases as catalysts and in our case the selectivity for the condensation product **3** was

100%. From a more quantitative point of view the results from table 2 indicate that the order of reactivity of the catalysts tested is ALPON-3 > MgO > HT-2. This was the expected order considering a previous work [16,17] on the Knoevenagel condensation of methylenic active compounds with different pK_as, where it was found that the number of basic sites in ALPON samples with a nitrogen content $\geqslant$5% is larger than in MgO and HT, while the basic sites on MgO and HT are stronger than on ALPON.

For comparison purposes, we have carried out the synthesis of α-methylbenzylidenemalononitrile (**3**) using a mixture of acetic acid–ammonium acetate as catalyst at reflux of benzene. After 8 h of reaction time the yield of **3** was 34%. Then, from the results presented above, we can conclude that ALPON materials are more adequate to carry out the first reaction step than the conventional acetic acid–ammonium acetate catalyst.

However, it is known that in ALPON materials it is possible to modify the number and strength of the active sites by changing the chemical composition. In fact, it has been shown that it is possible to modify the level of nitrogen content by changing the nitridation conditions, and the amount of nitrogen incorporated not only has an influence on the total number of actives sites but also on their basic strength [16]. Up to now the nature of the aluminophosphate oxynitride basic sites is not yet exactly known, but IR [16], DRIFT, XPS [20], and magic angle spinning NMR studies [21] have shown that basic sites such as –NH–, –NH_2 and even strongly adsorbed NH_3 are created by nitridation, and their proportion changes with the amount of nitrogen content or, even better, with the treatment conditions.

In order to optimise the catalytic activity of the ALPON catalysts for the Knoevenagel reaction between acetophenone (**1**) and malononitrile (**2**) we have prepared samples with different nitrogen contents, within a range between 0 and 13.7 N wt%, and the initial reaction rates as well as the yields of **3** obtained after 3 h reaction time are summarised in table 2. The results from this table indicate that the activity of the ALPON increases when increasing the amount of nitrogen in the catalyst. Moreover, when the initial rates are plotted *versus* the nitrogen content of the catalysts, a linear correlation is obtained (figure 1) indicating that all basic sites produced at different levels of nitrogen content were equally active for carrying out this condensation. These results agree with previous work, where a similar behaviour has been shown for reactions which are not highly demanding from the point of view of basicity, *i.e.*, Knoevenagel condensation between benzaldehyde and malononitrile [16], ethyl cyanoacetate [16], or arylsulfones [19].

3.2. Synthesis of 1,1-dicyano-2,4-diphenyl-1,3-butadiene (5)

In the second part of this work, the preparation of 1,1-dicyano-2,4-diphenyl-1,3-butadiene (**5**) was carried out by condensation of **3** with benzaldehyde (**4**) (scheme 1(B)). This reaction is more demanding from the point of view of the basic strength needed, since the abstraction of the proton from the methyl group of compound **3** is more difficult than in the case of malononitrile.

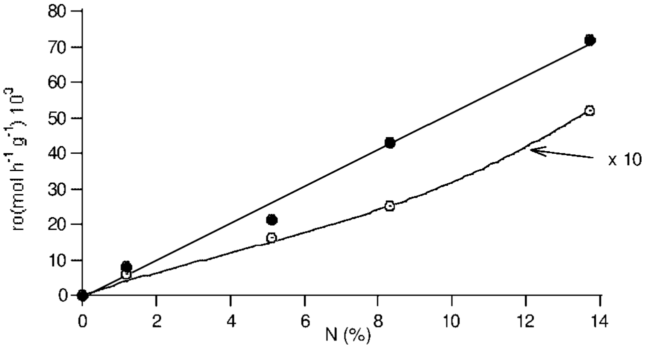


Figure 1. Initial rates (r_0) *versus* nitrogen content plot for the condensation of (**1**) (7.5 mmol) and (**2**) (7.5 mmol) at 373 K (•) and for the condensation between **3** (4 mmol) and **4** (4.4 mmol) at 398 K (○) in the presence of ALPON catalysts (5 wt%).

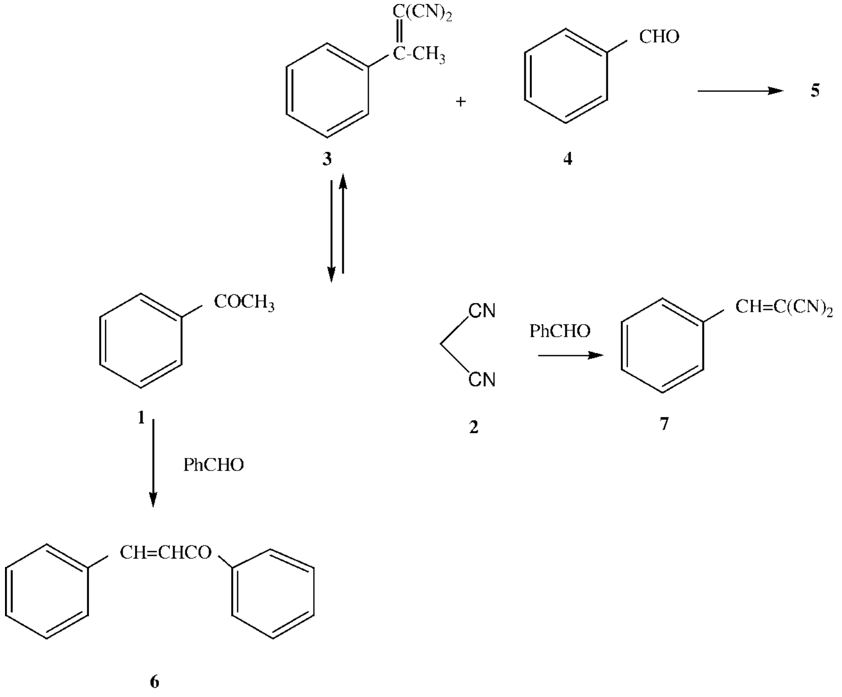
Table 3
Condensation of α-methylbenzylidenemalononitrile (**3**) and benzaldehyde (**4**) on different basic catalysts (5 wt%) without solvent at 398 K.

Catalyst	Yield of **5**[a] (%)	Selectivity to **5**	Other[c] **1**	**6**	**7**
ALPON-0	–	–	–	–	–
ALPON-1	5	100	–	–	–
ALPON-2	12	100	–	–	–
ALPON-3	20	100			
ALPON-4	25	96[c]	–	–	–
HT-1	37	88	3	1	1
HT-3	17	89	2	–	–
MgO	10[b]	20	35	3	2

[a] 14 h reaction time.
[b] 7 h reaction time.
[c] Traces of the compound coming from the condensation of **3** with acetophenone were also detected.

As we have indicated earlier, in the case of ALPON catalysts the number of active sites and their basic strength depend on the amount of nitrogen incorporated. Then, in order to check the influence of the nitrogen content of the ALPON on their catalytic activity for the condensation between **3** and benzaldehyde, we have carried out the reaction in the presence of ALPON with different amounts of nitrogen incorporated. In table 3 the results obtained with these catalysts are given.

From the results in table 3 it is possible to conclude that the number of active sites with enough basic strength to perform the condensation between **3** and **4** is lower than the number of sites able to carry out the Knoevenagel condensation between acetophenone and malononitrile. Moreover, when the initial reaction rate was plotted *versus* the nitrogen content a linear increase of activity with the nitrogen content of the catalyst can be observed. However, it appears that at higher nitrogen content the variation of activity with nitrogen content can be exponential. If this is so, it may indi-

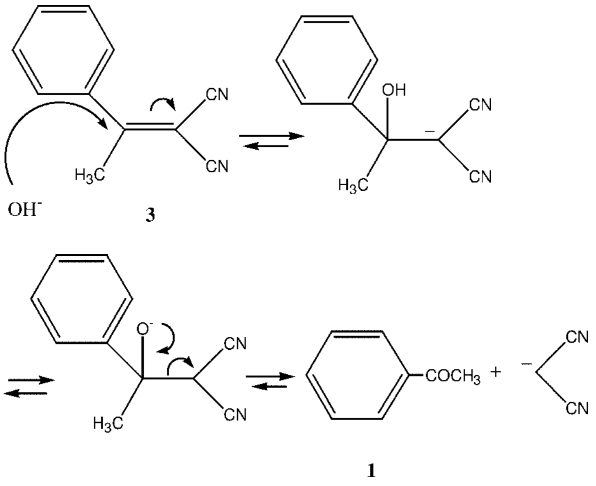


Scheme 2.

cate that the proportion of the stronger basic sites required to catalyse this reaction increases with the nitrogen level (figure 1). However, at the reaction conditions tested, even the sample containing the largest amount of N content yields only a 25% of the dye product after 14 h of reaction time. From the preparative point of view it appears that this yield is too low. Nevertheless, it is interesting to notice that with the procedure reported in the literature using acetic acid–ammonium acetate as catalysts at reflux of benzene the yield obtained was very similar but with a much more complicated work-up.

At this point, if one wants to increase the yield of dye it seems logical to go into solid catalysts with higher basic strength. Hydrotalcite-derived mixed oxides could be adequate catalysts for this reaction because of their high surface area, phase purity, structural stability [22], and the fact that calcined Al–Mg-hydrotalcites have basic sites able to abstract protons from reactants with pK_a up to 16.5 [13,23], and consequently they are able to catalyse effectively aldol condensations involving acetone or acetophenone, with benzaldehyde at moderate temperatures [15,23–25]. On calcined magnesium–aluminium hydrotalcites the surface acid–base properties and consequently the catalytic activity and selectivity depend on the calcination temperature and the Mg/Al ratio. Therefore, a hydrotalcite with a defined Mg/Al composition may show unique catalytic properties depending on the reaction requirements for the density and strength of basic sites.

In order to check the activity and selectivity of calcined Al–Mg, hydrotalcites, as well as the influence of their chemical composition on the condensation of **3** with **4**, we selected three samples with Al/(Al + Mg) atomic ratios of zero (MgO), 0.20 (HT-1), and 0.33 (HT-3).



Scheme 3.

It is known that calcined hydrotalcites stored in air partly lose their activity due to the adsorption of CO_2 from the atmosphere. Therefore, the samples were reactived by heating in vacuum at 698 K before use. With both hydrotalcite catalysts acetophenone (**1**), chalcone (**6**), and benzylidenemalononitrile (**7**) (scheme 2) were also detected in the reaction mixture, the selectivity to product **5** on the two hydrotalcites being approximately 90% (table 3). Taking into account that the experiments were carried out starting with purified **3** compound, the presence of acetophenone as well as products **6** and **7**, which arise from the condensation of benzaldehyde with acetophenone and malononitrile, respectively, indicates that under our reaction conditions the retro-Knoevenagel reaction of the reactant **3**, although in little extent, is taking place (schemes 2 and 3).

In table 3 it is possible to see that the calcined hydrotalcite sample with lower Al/(Al + Mg) ratio (HT-1) presents two times higher activity than HT-3 with a higher Al content. This result is in good agreement with the fact that the incorporation of aluminium into MgO forming Al_2O_3–MgO oxides after calcination of hydrotalcites decreases the total number of basic sites, but increases the proportion of stronger ones [26]. Then, hydrotalcites have basic sites strong enough to catalyse this reaction but if the Al content is too high, the presence of stronger basic sites as consequence of the larger aluminium content in the HT-3 sample, does not compensate the decrease of the total density of basic sites.

When the reaction was carried out in presence of MgO, which possesses a higher density of basic sites but with lower basic strength with respect to calcined hydrotalcites, a surprising result was obtained. In this case, the retro-Knoevenagel condensation of the reactant **3** is favourably competing with their condensation with benzaldehyde. A total conversion of 50% was achieved after 7 h reaction time, but the yield of the dye **5** was only of 10%, the selectivity to the desired product (**5**) being 20%. In this case acetophenone (35% of yield) is the main product, but small amounts of the **6** and **7** were also detected during the reaction (table 3) (scheme 2). These results may indicates that under our experimental conditions the water present, coming from the condensation between **3** and **4**, reacts with strong and medium strong basic sites on the surface of MgO producing a high concentration of OH^- groups. Meanwhile, it is observed that the rate of the decomposition of the Knoevenagel adduct (**3**) is higher than the rate of condensation between **3** and **4**. Then, we can suppose that in the presence of a high concentration of accessible hydroxyl groups, the attack of the OH^- on the conjugate unsaturated system of compound **3** (scheme 3) should be favoured *versus* the abstraction of a proton from the methyl group which yields **5** as the final product. This hypothesis is supported by the fact that when the condensation reaction between **3** and benzaldehyde was carried out using a solution of 5% of KOH in ethanol at room temperature, after 72 h of reaction, the total conversion of **3** was 46% and the yields of acetophenone and **5** were 31 and 15%, respectively.

In the case of MgO and Mg–Al oxides derived from hydrotalcites, the basicity is associated with the presence of hydroxyl groups and framework oxygens [27] and in principle a similar behaviour for both catalysts as concerns the selectivity should be expected; in fact the catalysts are always in contact with the water produced by the reaction. However, we think that in the case of calcined hydrotalcites, the so-called memory effect of these materials [28] could play a key role on their high selectivity observed for the product **5**. It has been reported that in presence of water the lamellar structure can be restored, OH^- becoming the compensating anions and inducing strong basicity [15,29]. Then it is possible that the water produced during the condensation was removed from the medium by reaction with the calcined hydrotalcite. The higher water absorption of HT compared with MgO together with the fact that the free hydroxyl groups, capable to act as nucleophilic species and to produce the retro-Knoevenagel process are located between the layers, very few of them being accessible to reactants, should explain the lower activity of HT for the retro-Knoevenagel reaction. Furthermore, the reaction between **3** and benzaldehyde should be occurring by a reaction between the carbanion produced from the reaction of **3** with a basic site and the adsorbed aldehyde [30] and it has been reported that the absorption of benzaldehyde on hydrotalcites is stronger than on MgO due to the higher basicity of the former [15]. We thought that these two facts could explain the higher selectivity of hydrotalcites than MgO towards the formation of the desired 1,1-dicyano-2,4-diphenyl-1,3-butadiene (**5**) product.

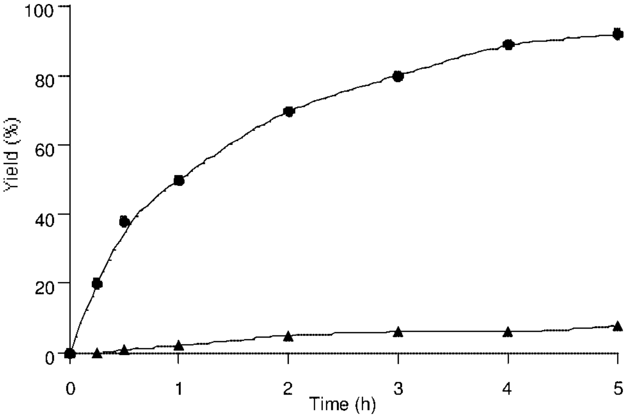


Figure 2. Condensation between **3** (5 mmol) and **4** (12.5 mmol) in the presence of ALPON-4 (10 wt%) at 423 K. **5** (●) and **1** + **6** + **7** (▲).

On the other hand, and from the preparative point of view, one has to take into account that there are not very significant differences between the final yields of the dye **5** obtained on HT-1 and ALPON-4 (table 3), the ALPON catalyst being more selective to the dye. Moreover, ALPON catalysts present the advantage that they do not need a previous reactivation step before use. Because of that, and in order to improve the final yield of **5**, we chose ALPON-4 as catalyst and we did the reaction between **3** and **4** at 423 K, in the presence of a 10 wt% of ALPON-4 and using a **4**/**3** molar ratio of 2.5. The results obtained after 5 h reaction time are presented in figure 2. It can be seen that it is possible to achieve a 100% conversion of **3** with a selectivity of 93% to **5**; 7% of by-products **1**, **6**, and **7** were also detected. These results are far better that what can be achieved by using ammonium acetate and glacial acetic acid as catalyst.

However, from a practical point of view it will be more interesting to perform the two-step process in one pot. In order to test this possibility, the reaction between **1** and **2** was carried out at 373 K in presence of ALPON-4 until the yield of **3** was 90% (100% of selectivity) and then the convenient amount of benzaldehyde was added and the temperature raised up to 423 K, as has been described in the experimental section. After 6 h reaction time we obtained a conversion of **3** of 100% with a 92% yield of **5**. However, the unreacted acetophenone and malononitrile from the first step or produced by retro-Knoevenagel condensation of **3**, also react, yielding the corresponding condensation products (**6** and **7**). Then, the final molar composition of the mixture (without considering the excess of benzaldehyde) was: 76% of **5**, 7% of **1,** 5% of **6** and 8% of **7**.

4. Conclusions

It has been possible to replace the classical catalyst for the synthesis of dicyanomethylene derivative dyes, which is formed by ammonium acetate and glacial acetic acid, by more environmentally friendly solid base catalysts.

Among hydrotalcites and ALPON, the latest has given very high activity and selectivity for the first step of the reaction studied here and which yields α-methylbenzylidenemalononitrile. This was used as reactant for the second reaction step to produce the final dye, 1,1-dicyano-2,4-diphenyl-1,3-butadiene, the reaction being catalysed by hydrotalcites and ALPON.

MgO was not a good catalyst for the second reaction step since, under our reaction conditions, it preferentially catalyses the retro-Knoevenagel condensation of the product formed in the first reaction step (**3**).

It was possible to carry out the two steps in "one pot" reaction with good conversions and fair selectivities using an optimised ALPON as catalyst.

The solid base catalyst studied here presents clear advantages over the catalyst used up to now, *i.e.*, ammonium acetate and glacial acetic acid.

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