New Aspects of Knoevenagel Condensation and Michael Addition Reactions on Alkaline Carbonates

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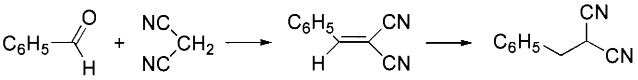
The Knoevenagel condensation of malononitrile with benzaldehyde on K_2CO_3, Rb_2CO_3 and Cs_2CO_3 gave the condensation product benzylidenemalononitrile but the reaction proceeded to the hydrogenated product benzylmalononitrile. Also, the Michael addition of malononitrile to certain double bonds occurs in the presence of K_2CO_3.

Basic catalysts are receiving much attention lately as they facilitate a variety of organic reactions useful in fine chemistry processes.[1-3] The Knoevenagel reaction has been shown to take place on various basic solids.[4,5] With some catalysts, a Michael addition reaction occurs as well. Both steps involve the catalyst's basic sites and have been shown to produce surface carbanions.

Alkaline carbonates have recently started to be used as catalysts and other types of agents in organic syntheses. Thus, Cs_2CO_3 forms cesium oxalate from a mixture of CO and CO_2.[6] Also, Ullman syntheses for diaryl ethers are catalysed by K_2CO_3 in the presence of CuI as co-catalyst.[7] Alkaline carbonates can also catalyse Knoevenagel reactions, where the rate of formation of product has been found to be highly correlated with carbonate alkalinity.[8] This paper reports results obtained in the condensation of malononitrile (MLN) and benzaldehyde (BZ) when the reaction is allowed to proceed beyond the time required for complete conversion to the condensation product. Also, results of the addition of malononitrile to double bonds in the presence of K_2CO_3 are reported.

The following commercially available alkaline and alkaline earth carbonates were used: Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3, $CaCO_3$, $SrCO_3$, and $BaCO_3$. Prior to use, all solids were subjected to the following stepwise calcination programme: 1 h at 200 ºC, 1 h at 300 ºC, 1 h at 400 ºC, and 1 h at 500 ºC. The TGA and XRD patterns obtained after calcination showed that none of the carbonates had decomposed over the temperature range studied. Also, their S_{BET} never exceeded 2 $m^2\ g^{-1}$. Knoevenagel reactions were conducted in a flask that was fitted with a reflux condenser and filled with a mixture of 15.88 mmol of freshly distilled benzaldehyde, 47.46 mmol of malononitrile, and 24 mL of 1,4-dioxane solvent. After heating to 90 ºC, 0.546 g of the carbonate was added (t = 0). Michael addition reactions were carried out in a similar way, by using an equimolar mixture (15.88 mmol) of malononitrile and one of the following alkenes: *trans*-β-methylstyrene, methyl *trans*-cinnamate, *trans*-β-nitrostyrene, and diethyl fumarate. Portions of the reaction mixture were subsequently withdrawn periodically for gas chromatographic analysis using an SPB-5 60 m × 0.25 mm ID phenyl silicone capillary column and raising the temperature from 150 to 280 ºC at 15 ºC min^{-1}. The identity of each reaction product was confirmed by ^1H-NMR and MS. The gases released during the reaction were monitored by fitting the reactor outlet with a VG Sensorlab mass spectrometer.

The variation of the concentration of the reaction products with time revealed the following sequence of catalytic activity: $CaCO_3$, $SrCO_3 < Li_2CO_3 < BaCO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$.[8] Thus, the activity increased with increasing radius of the cation in the carbonate (i.e. with increasing electronegativity). A similar sequence was previously found for X and Y zeolites exchanged with lithium, sodium, potassium and cesium.[4] However, if after the condensation product benzylidenemalononitrile **1** was formed, the reaction was allowed to proceed, the hydrogenated product benzylmalononitrile **2** was obtained. Product **2** was only formed in the presence of K_2CO_3, Rb_2CO_3 or Cs_2CO_3, but not in that of the other carbonates.



1 **2**

An analysis of the reaction mixture during the additional time revealed the presence of tetracyanoethylene (TCNE) in the medium, which suggests that the hydrogen needed for the reduction comes from malononitrile. Also, the solid, which had so far remained unaltered as a carbonate, underwent a major transformation and released CO_2 during the reaction. Skarzewski and Zon[9] reported on the oxidative coupling of dimethyl malonate to tetramethyl ethene-1,1,2,2-tetracarboxylate using a cerium ammonium nitrate/magnesium oxide catalyst. The reaction does not take place in the absence of MgO. They proposed a reaction scheme where malonate ions formed on the MgO surface react with malonyl radicals produced at an oxidizing surface site. Other instances of oxidative coupling for

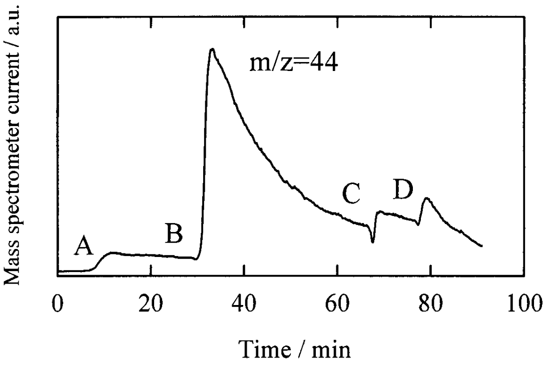


Figure 1. Monitoring of CO_2 on successive addition of: (A) 2 mL of MLN + 1.092 g of K_2CO_3 + 20 mL of 1,4-dioxane; (B) 1 mL of MLN + 2.45 g of compound **1** + 15 mL of 1,4-dioxane; (C) 1 mL of MLN + 5 mL of 1,4-dioxane; (D) 0.2 g compound **1** + 0.2 mL 1,4-dioxane.

unsubstituted malonates on $I_2/KF/Al_2O_3$ and by electrochemical means have also been reported. In an experiment with K_2CO_3, we mixed the reactants under different conditions and analysed the gases released (Figure 1). As can be seen, addition of further compound **1** to the reaction medium caused CO_2 production to increase considerably, concomitantly with an increase in the concentration of compound **2** in the reaction medium. At the same time, the solid was gradually converted into the oxide and dissolved in the reaction medium as the hydrogenation progressed. Alkaline and alkaline earth carbonates which only gave benzylidenemalononitrile did not decompose. Figure 2 shows the variation of the selectivity towards reaction products (100 × conversion towards a product / percentage overall conversion of benzaldehyde) with time. At the end, product **1** had been fully converted into **2**.

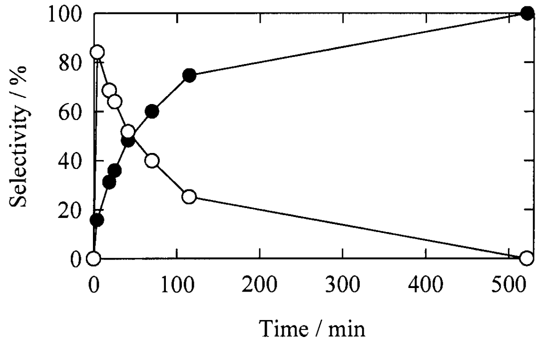
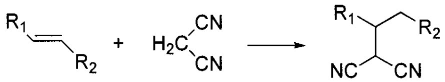


Figure 2. Variation of the selectivity towards compounds **1** (○) and **2** (●) with reaction time using solid K_2CO_3.

No other product such as benzoic acid or benzyl alcohol was detected in the reaction medium. When the reaction was carried out at a malononitrile/benzaldehyde ratio of 1:1, the mole ratio of compounds **1** to **2** was 1.52, 1.85 and 2.50 (at t = 120 min) in the presence of K_2CO_3, Rb_2CO_3 and Cs_2CO_3, respectively.

The fact that the hydrogenation step occurred with the K, Rb and Cs carbonates appears to be related to the weaker M–O bond of these compounds (a result of the larger size of their metal ions).[10] Probably, surface M–OH and M–H species are formed by decomposition of the carbonates, which would be similar to those proposed by Kibby and Hall for the dehydrogenation of alcohols over hydroxyapatite.[11] In this case, the hydrogen is abstracted from the alcohol and can be subsequently transferred to a carbonyl compound. The presence of TCNE suggests that a dicyanocarbene occurs as an intermediate species.

Table 1. Reaction of malononitrile with several alkenes in the presence of K_2CO_3



R_1	R_2	Yield / %
C_6H_5	CH_3	-
C_6H_5	$COOCH_3$	35
C_6H_5	NO_2	71
$COOC_2H_5$	$COOC_2H_5$	77

On the other hand, we considered the application of these carbonates to other processes. Some preliminary results are given in Table 1. As can be seen, malononitrile can be added to certain double bonds in the presence of K_2CO_3. Interestingly, electron-withdrawing groups favor the reaction. Thus, no reaction was observed with cyclohexene or *trans*-β-methylstyrene. The regioselectivity achieved in the reaction suggests a Michael addition mechanism.[12]

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References

1 H. Hattori, *Chem. Rev.*, **95**, 537 (1995).
2 A. Corma, S. Iborra, S. Miquel, and J. Primo, *J. Catal.*, **173**, 315 (1998).
3 M. J. L. Gines and E. Iglesia, *J. Catal.*, **176**, 155 (1998).
4 A. Corma and R. M. Martín-Aranda, *Appl. Catal.*, **105**, 271 (1993).
5 J. A. Cabello, J. M. Campelo, A. García, D. Luna, and J. M. Marinas, *J. Org. Chem.*, **49**, 5195 (1984).
6 K. Kudo, F. Ikoma, S. Mori, K. Komatsu, and N. Sugita, *J. Chem. Soc., Chem. Commun.*, **1995**, 633.
7 K. Smith and D. Jones, *J. Chem. Soc., Perkin Trans. 1*, **1992**, 407.
8 M. A. Aramendía, V. Borau, C. Jiménez, J. M. Marinas, and F. J. Romero, *Chem. Lett.*, **1995**, 279.
9 J. Skarzewski and J. Zon, *Synth. Commun.*, **25**, 2953 (1995).
10 W. A. Hart, O. F. Beumel, Jr., and T. P. Whaley, "The Chemistry of Lithium, Sodium, Potassium, Rubidium, Cesium and Francium," Pergamon Press, Oxford (1975).
11 C. L. Kibby and W. K. Hall, *J. Catal.*, **31**, 65 (1973).
12 J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," 3rd ed., Wiley, New York (1985).