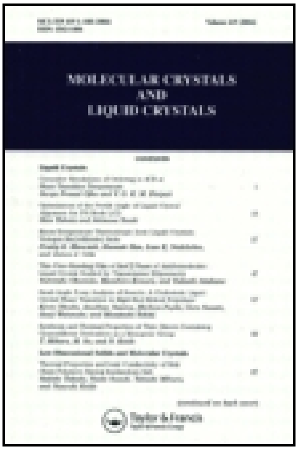

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Intracrystalline Pinacol Rearrangement in Layer Silicates

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INTRACRYSTALLINE PINACOL REARRANGEMENT IN LAYER SILICATES

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Abstract The selectivity of some reactions of substituted 1,2-glycols adsorbed in the interlayer space of layer silicates (homoionic montmorillonites) has been studied. By thermal treatment, pinacol rearranges quantitatively to pinacolone in the intracrystalline environment of these solids, the reaction being clearly preferred to the intramolecular dehydration. In the same way 2,3-diphenyl-2,3-butanediol gives two ketones, the reaction being also different from that taking place in homogeneous conditions. The extent and the selectivity of both reactions have been correlated with the acidity of the interlayer cations.

INTRODUCTION

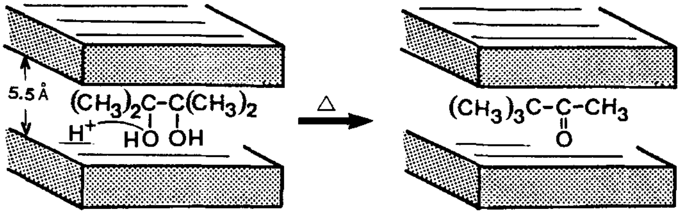
The use of solid inorganic supports for organic synthesis has recently received a great deal of interest because the selectivity of the reactions is often enhanced with respect to the same ones carried out in homogeneous conditions[1]. The topology as well as the nature of the surface of the solids are determining factors for the development and yield of the reactions[2]. In particular, layered materials, as the 2:1 phyllosilicates, can induce selective reactions, although only in a few cases has it been clearly demonstrated that they occur in the intracrystalline environment[3].

RESULTS AND DISCUSSION

We have found, and report in this communication, that the pinacol rearrangement[4] of substituted 1,2-glycols can be developed in the interlayer space of certain phyllosilicates (homoionic montmorillonites[5]). Thus, the intercalation of pinacol (2,3-dimethylbutane-2,3-diol, I) and the subsequent thermal treatment induces a selective and quantitative rearrangement to pinacolone (3,3-dimethylbutane-2-one, II), this process being preferred to the intramolecular dehydration to 2,3-dimethyl-1,3-butadiene (III). We also report here results concerning to 2,3-diphenyl-2,3-butanediol (IV) which in the presence of M^{n+}-montmorillonite rearranges selectively to 3,3-diphenylbutan-2-one (V) and 1,2-diphenyl-2-methyl-1-propanone (VI), showing a marked difference with respect to the same reactions carried out in homogeneous conditions.

It is well known that polar organic molecules (alcohols, amines, ketones,...) can be adsorbed in the interlayer space of phyllosilicates[6]. In this way, we have observed that compound I is easily intercalated[7] in M^{n+}-montmorillonites (M^{n+}= Na^+, Ca^{2+}, Cu^{2+}, Cr^{3+}, Al^{3+}, La^{3+}), the interlayer distances of the silicate being near to 5.5 Å[8]. This value agrees with the thickness of the pinacol molecule and, taking into account the adsorbed amounts ($\sim 1.10^{-3}$ mole.g^{-1}), it can be determined that a monolayer of I is reached.

By thermal treatment of the M^{n+}-montmorillonite/pinacol system, the rearrangement reaction of I to II is observed, and we can assume that an acid-catalysed process takes place according to Eq. (1), the source of protons being the water molecules coordinated to the interlayer cations. In fact, it is well known that the degree of dissociation of adsorbed



I II (1)

water is correlated with the polarizing effect of the M^{n+} ions[9] (Eq. (2)).

$$|M(H_2O)_x|^{n+} \rightleftharpoons |M(H_2O)_{x-1}OH|^{(n-1)+} + H^+ \qquad (2)$$

Thus, we can suppose that in a first step, a proton transfer reaction to I occurs followed by the formation of a carbonium ion which becomes stabilized by the migration of CH_3- groups giving product II, in a similar mechanism to that accepted for homogeneous conditions[4].

The second example refers to compound IV. In homogeneous conditions (conc. H_2SO_4, reflux) this compound is transformed to an unique carbonylic product (V) with a yield of ∿50%[10]. However, when the reaction takes place in the presence of M^{n+}-montmorillonite, the rate of conversion is significantly enhanced and, besides, two reaction products (V and VI) instead of one (V) are isolated, as is illustrated in Eq. (3). The formation of byproducts (for example the conjugated olefin) is negligeable in these conditions.

$$\underset{\text{IV}}{|(CH_3)PhC(OH)|_2} \longrightarrow \underset{\text{V}}{(CH_3)Ph_2CCOCH_3} + \underset{\text{VI}}{(CH_3)_2PhCCOPh} \qquad (3)$$

The yield of the two reactions studied in this work (determined by GC/MS and IR techniques) depends strongly on the experimental conditions (time, temperature) as well as on the nature of the M^{n+} cations. In particular, a good correlation between the reaction yield and the acidity (electronegativity or ionic potential)[11] of the interlayer cations has been found (Table I).

TABLE I Rates of conversion of I and IV compounds adsorbed on M^{n+}-montmorillonites.

		Transformation of I^b (%)			Transformation of $IV^{d,e}$ (%)	
M^{n+}	Z/r^a	I^c	II	III	V	VI
Na^+	1.05	83	10	6	91	5
Ca^{2+}	2.02	84	13	3	60	9
Cu^{2+}	2.90	18	78	3	81	17
La^{3+}	2.61	26	72	0	54	46
Cr^{3+}	4.35	0	99	0	30	70
Al^{3+}	6.00	0	98	0	29	70

[a] Z/r=ionic potential[11]: Z=cation charge; r=ionic radius. r values taken from L. Pauling, The nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1960). [b] After a treatment of 1h at 100°C. [c] Unreacted pinacol. [d] After a treatment of 15h at 160°C. [e] For $M^{n+} = Ca^{2+}$, the conjugated olefin is also isolated (28%).

CONCLUDING REMARKS

The most significant results of this work concern the selectivity of the reactions: in the transformation of I, the II/III ratio increases clearly as a function of the acidity of the M^{n+} cations, and in the transformation of IV, the

V/VI ratio changes also strongly with the nature of the M^{n+} ions. In the last case, one can suppose that the geometrical limitations existing in the interlayer space will condition the migratory aptitude of methyl and phenyl groups, favouring certain molecular configurations of the reaction products that can be different from those adopted in solution. Further investigations related to intracrystalline reactions of 1,2-glycols are in progress, aiming mainly to elucidate the mechanism and the selectivity of the processes.

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5. Montmorillonites that belong to the family of 2:1 phyllosilicates, are structurally constituted by the superimposition of layers,each one consisting in a central octahedral sheet of Al^{3+} or Mg^{2+} ions condensed with a sheet of silica tetrahedra on each side. The layers are negatively charged due to isomorphous substitutions. This charge is compensated by hydrated cations (exchangeable cations, M^{n+}) in the interlayer space. Montmorillonite from Upton (Wyoming, USA) with a cation exchange capacity of $\sim$90 meq/100 g and microcrystalline particles <2μ, has been used in this work.
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7. Films of homoionic montmorillonites were treated at 25°C by concentrated solutions of the glycol in a solvent (methanol, chloroform), until the equilibrium of adsorp-

tion was reached.

8. The separation between the layers of the intercalated montmorillonite has been determined from the 001 rational reflections in the corresponding X-ray diffraction patterns.
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