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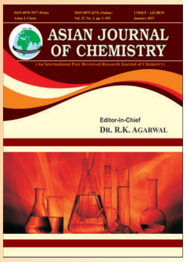
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Formation of Benzylidenes-Diacetates Catalyzed by Activated Zeolite "LZY-562" and Clay ($K10/ZnCl_2$): An Unexpected Functional Selectivity

H. DOKARI[1], M. HAMMADI[1], N. BENFERRAH[2,*] and Y. RACHEDI[3]

[1]Faculty of Sciences, UMBB, University of Boumerdes, 35000 Boumerdes, Algeria
[2]URMPE Research Unit for Materials, Processes and Environment, Faculty of Engineering Sciences, UMBB, 35000 Boumerdes, Algeria
[3]Faculty of Chemistry, USTHB, University of Bab Ezzouar, 16000 Alger, Algeria

*Corresponding author: E-mail: benferrahnassima@gmail.com

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Activated zeolites LZY-562 and clay montmorillonite K10 at room temperature without solvent catalyzes the synthesis of benzylidenes-diacetates from carbonyl compounds. A chemoselectivity was observed between aldehydes and ketones, between the different aldehydes and ketones as well.

Keywords: Montmorillonite $K10/ZnCl_2$, Zeolites LY-562, *gem*-Diacetates, Chemoselectivity, Carbonyl compounds.

INTRODUCTION

The benzylidenes-diacetates have attracted great interest in organic synthesis as an alternative to acetals for the protection of aldehydes because of their remarkable stability in neutral reaction media as well as towards aqueous acids[1]. The products resulted by the condensation of aldehydes with the acetic anhydride in the presence of catalytic acids are generally stable in the weakly basic milieu[2]. In addition to carbonyl protection, *gem*-diacetates derived from α,β-unsaturated aldehydes are useful precursors for the preparation of acetoxybutadienes[2], nitrofuroxazines[3] and vinyl acetates[4] which turn useful as dienes for Diels-Alder reactions. *gem*-Diacetates are useful as carbonyl surrogates for asymmetric synthesis[5,6] and for nucleophilic displacement reactions[7-9]. Numerous methods have been developed for the preparation of *gem*-diacetates[10]. 1,1-Diacetates (Acylals) are generally prepared from aldehydes and acid anhydrides using either Bronsted acids (typically sulphuric acid)[11-13] or Lewis acids (*e.g.* $ZnCl_2$ or PCl_3)[14-16]. However, these methods are often accompanied by long reaction times and low conversions.

We have reported the formation of a wide variety of useful compounds (acetals, oxathiacetals, dithioacetals, thiochromanes, enolthioethers)[17-19] by the reaction of carbonyl compounds with thiols catalyzed by clay (Mont $K10\text{-}ZnCL_2$) in refluxing toluene. The $K10/ZnCl_2$ clay is inexpensive and offers several advantages over the classical acids: strong acidity, no corrosive action, selectivity and easy work-up. In these reactions, the clay acts as a solid Lewis acid catalyst. To our best of knowledge, the chemoselectivity between aldehydes or between ketones in the formation of derivatives *gem*-diacetates has not been reported until now in the literature.

EXPERIMENTAL

Melting points (m.p) were identified with a [NETZSCH STA 409 PC]. The IR spectra were recorded as KBr pellets on [Jasco S-4000, FT-IR]. Proton NMR spectra (PMR) were determined on Brucker AC 250 (250 MHz, $CDCl_3$, Me_4Si). Spectrometer UV-visible spectra [λ_{max} log (ε)] were obtained with [spectrophotometer T60]. TLC Analyses were performed by using Kieselgel Schleicher and Shull F 1500 Ls 254 and Merck 60F 254.The grinding of products were carried out on a analytical grinder A 10 of Janke and Kenkel-IKA Labortechnik. The montmorillonite K10 was obtained from the firm of Sud Chemie. Zeolites (LZY562) as ammonium form were calcinated at 500°C under dry flow before use (Linde).

Preparation of zeolites exchanged H^+: 20 g of zeolite (LZY562) are placed in a 100 mL flask and then treated with a solution of NH_4Cl (0.1 M) previously prepared with deionized water. The stoppered flask is allowed to stand overnight at room temperature. The solid residue was recovered by filtration and then activated in a muffle furnace at 500 °C for 24 h. The zeolite in H^+ (H^+-ZY562) is stored in a dry container.

Preparation of montmorillonite K10 exchanged by Zn^{2+}: In a 250 mL flask, the montmorillonite K10 (20 g) was added to a solution of $ZnCl_2$ (0.2 mol) dissolved in 100 mL of distilled water. The reaction mixture was stirred for 24 h at room temperature. The suspension was washed twice with distilled water then centrifuged. The montmorillonite exchanged by Zn^{2+} was washed with methanol and recentrifuged. The solid was dried for 24 h in vacuum then finely ground. The final product was a clear beige colour.

Formation of *gem*-diacetates from carbonyl compounds: A mixture of aldehyde or ketone (30 mmol), acetic anhydride (30 mmol) placed in a 25 mL of beaker, is adsorbed in alumino-silicate acids (clay or zeolite during 10 h under room temperature. Dichloromethane (20 mL) is added to beaker to extract of solid catalyzer followed by filteration through Buchner funnel. The solvent is evaporated *in vacuo* using a rotative evaporator. The obtained solid is identified by spectroscopic methods.

***Bis*-(diacetoxy)methyl(benzene) (2a):** Prepared from benzaldehyde (30 mmol: 3.19 g), acetic anhydride (30 mmol: 3.06 g) in presence of H^+-LZY562 (3 g); yellow solid crystallized in ethanol; m.p. = 44 °C (lit.[15]: 45 °C); $C_{11}H_{12}O_4$; mol. mass = 208.21 g/mol; Yield: 73 %; UV-visible λ_{max} log (ε) (dioxane/H_2O) nm: 226, 257, 263; IR (KBr) cm^{-1}: 3106 (νCH arom), 1728 (νOCOCH$_3$), 1512 (νC=C), 730 (δCH arom); ^1H NMR ($CDCl_3$).δ: 2,18 (s, 6H, CH_3); 5,21 (s, 1H, CH); 7.18-7.97 (m, 5H, H arom); S.M *m/z* (%): $M^{+\bullet}$ = 208.

1,4-*Bis*(diacetoxy)methyl(benzene) (3a): Prepared from terephthaldehyde (30 mmol: 4.02 g) acetic anhydride (30 mmol: 3.06 g) in presence of H^+-LZY562 (3 g); white solid crystallized in ethanol; $C_{16}H_{18}O_8$; mol. mass = 338.30 g/mol Yield: 71 %, IR (KBr) cm^{-1}: 2972 (νCH) (1731 (νOCOCH$_3$), 1450 (νC=C), 730 (νCH arom); ^1H NMR ($CDCl_3$) δ: 2.21 (t, 12H, CH_3); 5.23 (s, 2H, CH); 7.40 (m, 4H, H arom).

***Bis*(diacetoxy)methyl(4-acetoxylbenzene) (4a):** Prepared from 4-hydroxybenzaldehyde (30 mmol: 3.66 g) acetic anhydride (30 mmol: 3.06 g) in presence of clay K10/$ZnCl_2$ (3 g); white solid crystallized in ethanol; m.p. = 90 °C: $C_{13}H_{14}O_6$; mol. mass = 266.24 g/mol; Yield: 70 %, UV-visible λ_{max} log (ε) (dioxane/H_2O) nm: 252, 261; IR (KBr) cm^{-1}: 2948 (νCH-Arom), 1728 (νOCOCH$_3$), 1467 (νC=C), 860 (δCH, arom disustitued); ^1H NMR ($CDCl_3$) δ: 2.12 (s, 6H, CH_3); 2.22 (s, 3H, CH_3); 5.24 (s, 1H, CH); 7.18-7.97 (m, 4H, H arom).

***Bis*(diacetoxy)-methyl(4-chlorobenzene) (5a):** Prepared from 4-chlorobenzaldehyde (30 mmol: 4.22 g) acetic anhydride (30 mmol: 3.06 g) in presence of clay K10/$ZnCl_2$ (3 g); white solid crystallized in ethanol : m.p. = 81 °C; $C_{11}H_{11}O_4Cl$; mol. mass = 242.65 g/mol Yield: 69 %; UV-visible λ_{max} log (ε) (dioxane/H_2O) nm: 246, 253, 270, 274; IR (film) cm^{-1}: 3080, 2960, 1730 (νOCOCH$_3$) 1580, 940, 820, 727; ^1H NMR ($CDCl_3$) δ: 2.11 (s, 6H, CH_3); 5.25 (s, 1H, CH); 7.29-7.59 (m, 4H, H arom).

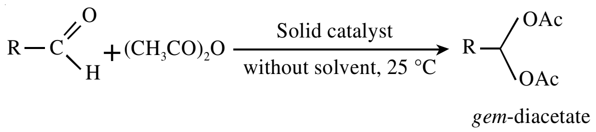
***Bis*(diacetoxy)-methyl(4-nitrobenzene) (7a):** Prepared from *p*-nitrobenzaldehyde (30 mmol: 4.53 g) acetic anhydride (30 mmol: 3.06 g) in presence of H^+-LZY562 (3 g); white solid crystallized in ethanol: m.p. = 125 °C(lit.[20]: 124 °C); $C_{11}H_{11}O_6N$; mol. mass = 221.21 g/mol Yield: 77 %, UV-visible λ_{max} log (ε) (dioxane/H_2O) nm: 260, 282; IR (film) cm^{-1}: 1732 (νOCOCH$_3$); ^1H NMR ($CDCl_3$) δ: 2.15 (s, 6H, CH_3); 5.24 (s, 1H, CH); 7.18-7.97 (m, 4H, H arom).

***Bis*(diacetoxy)-(methyl-phenyl)methane (10k):** Prepared from acetophenone (30 mmol: 3.60 g) acetic anhydride (30 mmol: 3.06 g) in presence of H^+-LZY562 (3g); yellow solid crystallized in ethanol: m.p. = 111 °C); $C_{12}H_{14}O_4$; MM = 222.23 g/mol; Yield: 68 %, UV-visible: λ_{max} log (ε) (dioxane/H_2O) nm, 264, 272; IR (film) cm^{-1}: 3060, 2940, 1725 (νOCOCH$_3$), 1729 (νOCOCH$_3$), 1470, 810.

Competition reactions between aldehydes and ketones: Equimolecular quantities of aldehyde and ketone, were dissolved in the minimum volume of methylene chloride mixed with one equivalent of acetic anhydride and adsorbed on to zeolite or montmorillonite Kio. The solvent was removed by evaporation *in vacuo*. All products were characterized by their IR and ^1H NMR spectra. Yields of products were determined by ^1H NMR spectroscopy.

RESULTS AND DISCUSSION

We report herein that the aldehydes react with one equivalent of acetic anhydride simply by adsorption on K10/$ZnCl_2$ or activated zeolites LY-562 at room temperature without solvent (**Scheme-I**).



Scheme-I: Intermolecular chemoselectivity

The results obtained for the synthesis of *gem*-diacetates are reported in Table-1. The yields of diacetates are excellent. In contrast with the results obtained in the homogeneous acidic phase, yields are also good with sensitive aldehyde such as thiophene-2-carbaldehyde (Yield: 80 %) dimethylamino-benzaldehyde (Yield: 78 %).

As far as the ketones are concerned, the conversion to *gem*-diacetates seems slower than that of the aldehydes in room temperature and lasts at least 20 h.

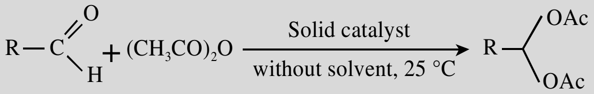
For instance, the cyclododécanone is converted to diacetate in 24 h; however, the reaction with light excess in refluxing happens in 10 h. The results of the ketones conversion to *gem*-diacetates are reported in Table-2 (**Scheme-II**).

The reaction is fast with aromatic aldehyde (10 to 12 h) but slower with aliphatic aldehyde and with ketones.

Competition reactions between aldehydes and ketones: Chemoselectivity between aldehydes and ketones was reported by Fazaeli *et al.*[20], Heravi *et al.*[21] and Wu *et al.*[21] using Kegging-type polyoxometalates. Ziyaei *et al.*[22] used lithium perchlorate in refluxing while Hajipour *et al.*[23] used P_2O_5/Al_2O_3. We have sought to exploit the kinetic difference in perspective of functional selectivity and its use in the soft competitive reactions between aldehydes and between ketones in the formation of derivatives 1,1-diacetates using solid alumino-silicates such as clay montmorillonite K10 or activated zeolites(H^+)-LZY562.

Qualitative kinetic results suggest the possibility of Intermolecular chemoselectivity. In a typical competitive experiment, an equimolar mixture (30 mmol) of benzaldehyde (**2**), acetophenone (**10**) and acid anhydride was adsorbed on K10/$ZnCl_2$ (3 g) at room temperature. After 24 h, the products were extracted with methylene chloride (20 mL) and the solvent was removed by evaporation *in vacuo*. Only the diacetate derivative of benzaldehyde was formed, in quantitative yield.

TABLE-1
CONVERSION OF ALDEHYDE TO 1,1-DIACETATES IN THE PRESENCE OF ACID ALUMINOSILICATES



gem-diacetate

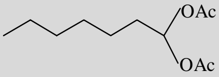
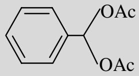
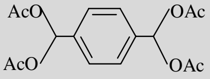
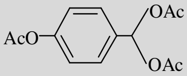
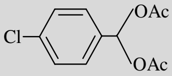
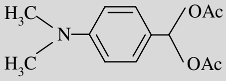
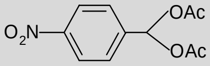
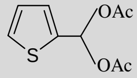
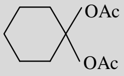
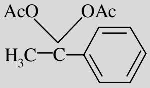
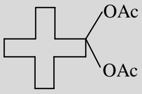
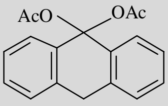
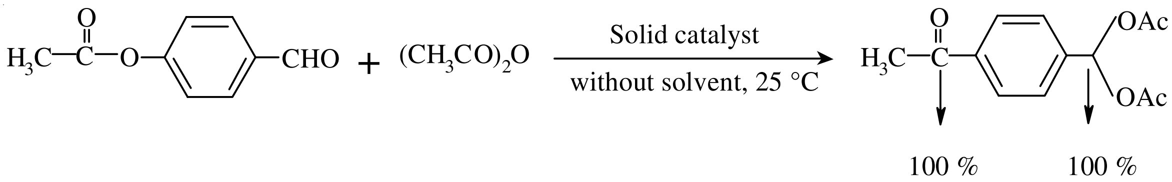
Aldehyde	Catalyst	Time (h)	Derivative diacetate	Yield (%)
Heptanal (**1**)	(H$^+$)-LZY562	20	 **[1a]**	51
Benzaldehyde (**2**)	(H$^+$)-LZY562	10	 **[2a]**	73
Terephthaldehyde (**3**)	(H$^+$)-LZY562	10	 **[3a]**	71
p-Hydroxybenzaldehyde (**4**)	K10/ZnCl$_2$	12	 **[4a]**	70
p-Chlorobenzaldehyde (**5**)	K10/ZnCl$_2$	12	 **[5a]**	69
p-Dimethylaminobenzaldehyde (**6**)	K10/ZnCl$_2$	11	 **[6a]**	78
p-Nitrobenzaldehyde (**7**)	(H$^+$)-LZY562	11	 **[7a]**	77
Thiophene-2-carbaldehyde (**8**)	(H$^+$)-LZY562	10	 **[8a]**	80

TABLE-2
CONVERSION OF KETONES TO 1,1-DIACETATES IN THE PRESENCE OF ALUMINOSILICATES ACID

Ketone	Solid catalyst	Time (h)	Derivative diacetate	Yield (%)
Cyclohexanone (**9**)	(H$^+$)-LZY562	24	 **[9k]**	51
Acetophenone (**10**)	K10/ZnCl$_2$	20	 **[10k]**	68
Cyclododecanone (**11**)	K10/ZnCl$_2$	24	 **[11k]**	60
Anthrone (**12**)	(H$^+$)-LZY562	20	 **[12k]**	70



Scheme-II: Intramolecular chemoselectivity

When the molecule contains several different carbonyl groups, as in 4-acetylbenzaldehyde (**13**), the only diacetate derivative formed with one equivalent of acetic anhydride is that of the aldehyde. The results obtained for the synthesis of diacetates are reported in Table-3.

We also observed chemoselectivity between aromatic aldehydes and aliphatic aldehydes. Only the aromatic diacetates was formed in competition reaction. The competitive reaction inter-aldehydes shows a noticeable and an unexpected chemoselectivity (Table-4).

TABLE-3
SELECTIVITY IN COMPETITION REACTIONS BETWEEN CARBONYL COMPOUNDS (A AND K) IN FORMATION OF BENZYLIDENES-DIACETATES (A' AND K')

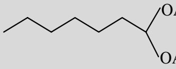
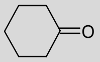
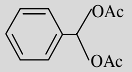
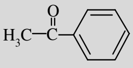
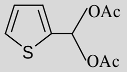
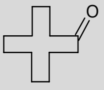
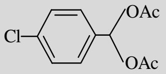
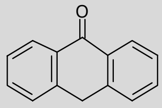
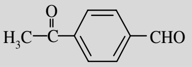
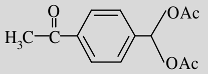
Carbonyl compounds		(Selectivity)	
Aldehyde	Ketone	A' [100 %]	K' [0 %]
(1)	**(9)**	 **[1a]** 100 %	 100 %
(2)	**(10)**	 **[2a]** 100 %	 100 %
(8)	**(11)**	 **[8a]** 100 %	 100 %
(5)	**(12)**	 **[5a]** 100 %	 100 %
 **(13)**		 **[13a]** 100 %	

TABLE-4
SELECTIVITY IN COMPETITION REACTIONS BETWEEN ALDEHYDES (A AND B) IN PRESENCE OF ACTIVE ZEOLITES (H^+)-LZY562

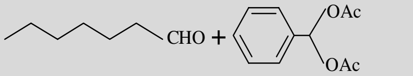
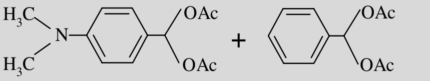
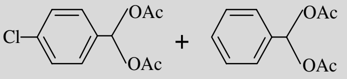
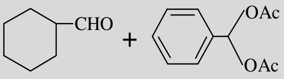
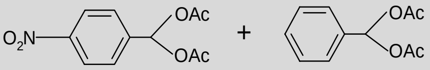
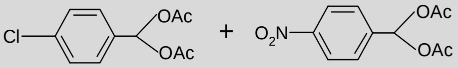
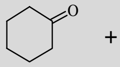
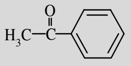
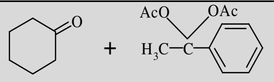
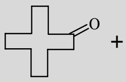
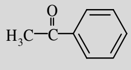
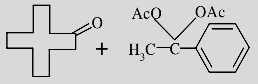
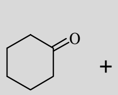
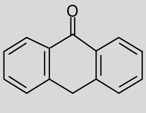
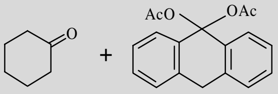
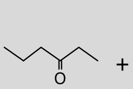
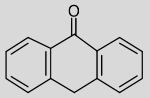
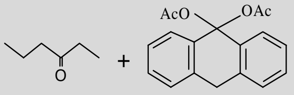
A	+	B	Selectivity
(1)		**(2)**	 100 % 100 % **[2a]**
(6)		**(2)**	 **[6a]** 57 % 43 % **[2a]**
(5)		**(2)**	 **[5a]** 55 % 45 % **[2a]**
(14)		**(2)**	 100 % 100 % **[2a]**
(7)		**(2)**	 **[7a]** 38 % 62 % **[2a]**
(5)		**(7)**	 **[5a]** 55 % 45 % **[7a]**

TABLE-5
COMPETITIVE REACTIONS BETWEEN KETONES IN PRESENCE OF K10 AT ROOM TEMPERATURE

Aliph. ketone	Arom. ketone	Selectivity
		 100 % 100 %
		 100 % 100 %
		 100 % 100 %
		 100 % 100 %

We also observed chemoselectivity between the ketones. Only aromatic diacetates was formed in competitive reaction after 24 h.

The competitive reaction between ketones is slow more than that of aldehydes (minimum 24 h) and shows a remarkable intermolecular chemoselectivity (Table-5).

Conclusion

Compared to conventional methods (homogeneous catalysis), all reactions were conducted at room temperature under favourable conditions. An unexpected functional selectivity was observed between different aldehydes or between aldehydes and ketones in the formation of derivatives *gem*-diacetates. The determinative effect is the presence or absence of aromatic rings. This may be related to the ease of aromatic molecules to slot between the aluminosilicate sheets. The lamellar nature of the montmorillonite clay as the phenomena of adsorption and desorption are for sure responsible for this selectivity.

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