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Friedel-Crafts benzylation of 1,4-dialkoxybenzenes – cleavage and rearrangement of esters and methoxymethyl ethers in $ZnCl_2$ montmorillonite K10 clay

C. Waterlot*, D. Couturier and B. Hasiak

Université des Sciences et Technologies de Lille, Laboratoire d'Ingéniérie Moléculaire, Bâtiment C4, 1er étage, 59655 Villeneuve d'Ascq Cedex, France

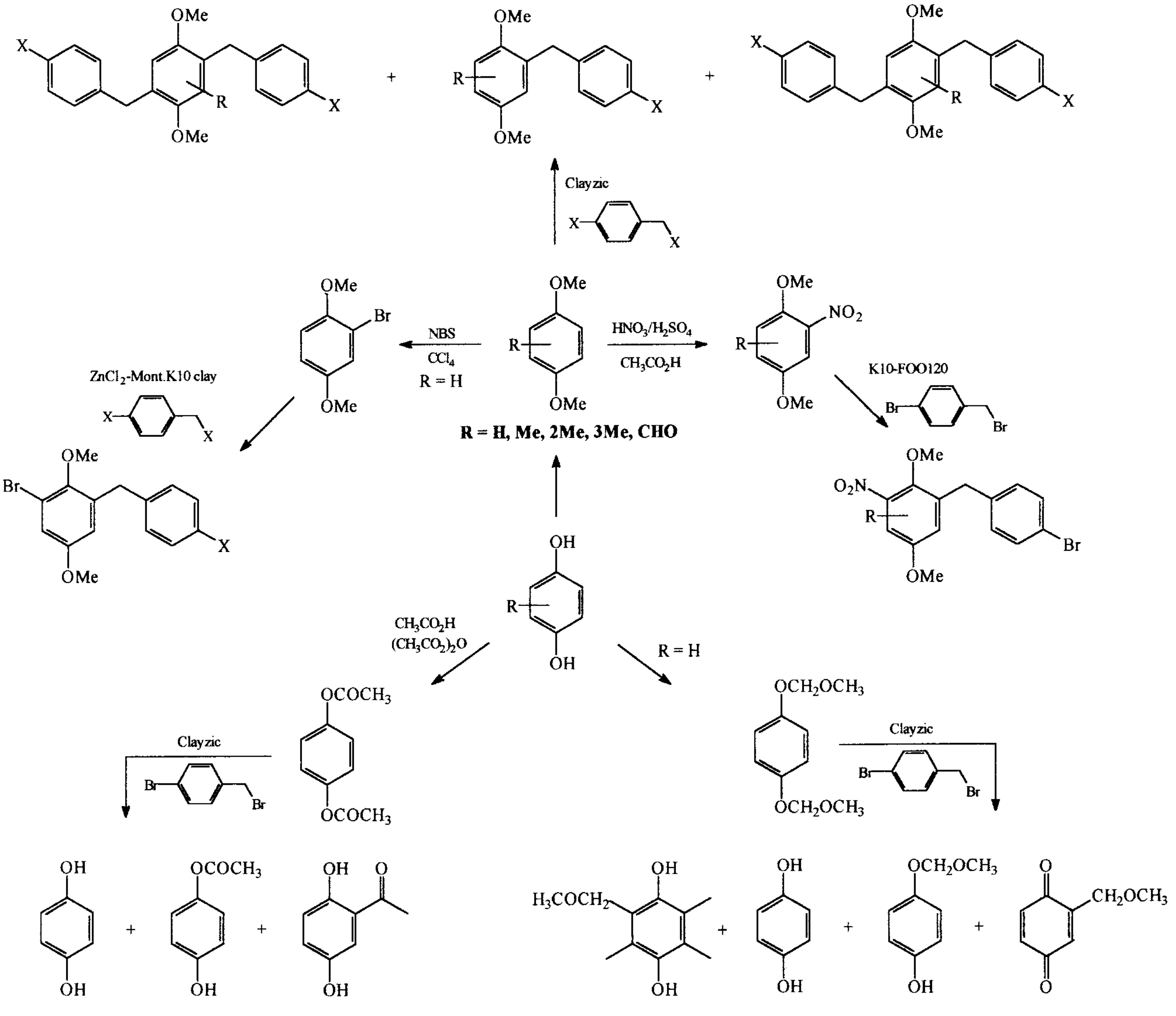
Benzylation of *p*-dialkoxybenzenes can be achieved through the use of modified montmorillonite K10 clay. For the first time, syntheses of nitro-diarylmethanes were obtained by Friedel-Crafts alkylation with good yields. In the case of *p*-methoxymethyl phenyl ether and phenyl ester, selectivity favoring Fries rearrangement over benzylation is reported.

Heterogeneous catalysts such as available commercially montmorillonite K10 clay, have been widely employed for the benzylation of arenes in recent years.[1,2] These inorganic materials are "environmentally friendly", inexpensive, easily recoverable and often show good selectivity. These properties are so very important when waste minimization is becoming a priority in many industries.

In connection to our interest in desoxygenation of dissolved oxygen from water, we investigated syntheses of diarylmethanes from 1,4-dialkoxybenzenes by using modified montmorillonite K10 clay as a catalyst. For the first time, alkylation of nitro-arenes yielding nitro-diarylmethanes and cleavage of *p*-methoxymethyl phenyl ether and phenyl ester are reported at room temperature

Results and discussion

Dimethoxydiarylmethanes were generally obtained with good yields (90%) by using Zn^{2+} exchanged montmorillonite K10 as catalyst ("Clayzic"). Only in the case of 1,4-dimethoxy-



Scheme 1

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* To receive any correspondence.

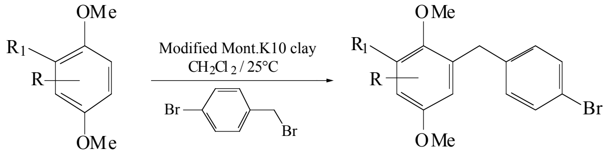
Table 2 Benzylation of nitro-arenes by using modified montmorillonite.K10 as catalyst

Entry	Compounds	R	Catalyst	Time (h)	**3a** (%)[d]	**3b** (%)[e]
1	1a	H[a]	Clayzic	5	4	–
2	1b	H	Clayzic	5	–	10[d]
3	1a	H	K10-ZnOO[b]	5	5	–
4	1b	H	K10-ZnOO[b]	5	–	20[d]
5	1a	H	K10-ZnOO120[b]	5	8	–
6	1b	H	K10-ZnOO120[b]	5	–	50
7	1a	H	K10-FeOO120[c]	5	15	–
8	1b	H	K10-FeOO120[c]	4	–	67
9	1a	Me[a]	K10-FeOO120[c]	4	–	63
10	1a	4,6-Me[a]	K10-FeOO120[c]	4	–	55

[a]Compounds were described in the literature[16]. [b]See the preparation in footnotes[15]. [c]The catalyst was prepared according S. G. Pai[14]. [d] Yields were determined by ^{1}H NMR and HPLC. [e]Isolated yields.

benzene as reactant, *p*-dibenzylation and *m*-dibenzylation were observed.

Because benzylation of 1-nitro-2,5-dimethoxybenzene **1b** (Scheme 2: R = H) yields only 10% of **3** (Table 2, entry 2) in the studied conditions, we thought that it could be interesting to investigate this reaction by using modified montmorillonite K10 clay. Results are summarized in Table 2.



1 **3**

1a $R_1 = CHO$ **3a** $R_1 = CHO$

1b $R_1 = NO_2$ **3b** $R_1 = NO_2$

Scheme 2

Results show that nitro-diarylmethanes can be synthesized with good yields by using the known K10-FeOO120 catalyst[14] (Table 2, entries 8, 9 and 10). On the other hand, alkylation of nitro-arenes is more efficient than alkylation of substituted benzaldehydes (compare Table 2, entries 5 and 6 or 7 and 8). According to the previous work[18], these results can be explain by an adsorption of nitro group on the active sites of the heterogeneous catalyst. From an industrial point of view, the methoxymethyl and acetoxy protective groups of diphenols have considerable interest because of the cleavage under mild conditions. We thought that it could be interesting to perform the benzylation of 1,4-diacetoxybenzene and 1,4-bis-(methoxymethyl)benzene diols with *p*-bromobenzylbenzene by using clayzic as catalyst. It was observed that no diarylmethane was formed during the reaction. On the other hand, results of mass spectra[23] showed that cleavage and rearrangement of ether and ester gave substituted hydroquinones. According to the previous work,[2,6] inhibition of the benzylation is due to the oxygen binding strongly onto the zinc catalytic centers of the heterogeneous catalyst.

In conclusion, we investigated the synthesis of diarylmethanes by using different heterogeneous catalysts. In that way, benzylation of nitro-compounds was reported. In the mean time, it was established that the presence of methoxymethyl or acetoxy groups hindered the benzylation reaction by using clayzic.

Techniques used: 1H and 13C NMR, IR, MS, CLHP

References: 24

Scheme 1

Scheme 3

Scheme 4

Scheme 5

Fig. 1 GC Traces of the crude obtained after benzylation of the 1,4-diacetoxybenzene **6**

Fig. 2 GC Traces of the crude obtained after benzylation of the 1,4-bis-(methoxymethyl)benzene diols **7**

Fig. 3 Structure of products formed during the benzylation of **6**

Fig. 4 Structure of products formed during the benzylation of **7**

Table 1: Benzylation of p-dimethoxybenzene by using clayzic as catalyst

Table 3: Benzylation of p-dimethoxybenzene by using clayzic as catalyst

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15 $ZnCl_2$ (10 g) and montmorillonite K10 (60 g) were added in dry methanol (100 mL). The resulting slurry was stirred at room temperature for 5 hours. The clay was then filtered, washed with dichloromethane (30 mL). The powder obtained was thermally activated overnight at 120°C. It is designated as K10-ZnOO120.

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