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Zeolites as Catalysts in Organic Reactions: Condensation of Aldehydes with Benzene Derivatives

MARÍA JOSÉ CLIMENT, AVELINO CORMA,[1] HERMENEGILDO GARCÍA,
AND JAIME PRIMO

*Instituto de Tecnología Química, CSIC-UPV, Universidad Politécnica de Valencia, Apartado 22012,
46071 Valencia, Spain*

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Reactions of four aldehydes with five aromatic compounds have been carried out on a series of USY zeolites with unit cell size in the 24.56 to 24.25-Å range. Conversion decreased in the order formaldehyde > benzaldehyde > acetaldehyde > propionaldehyde and also in the series anisole > toluene > benzene > chlorobenzene. For aliphatic aldehydes a mixture of *ortho–ortho'*, *ortho–para'*, and *para–para'* diarylmethanes was obtained. USY zeolites show a higher *para*-directing selectivity than $AlCl_3$. Benzaldehyde reacted with benzene derivatives to afford mixtures of diaryl- and triarylmethanes. Formation of ditolyl- and dianisylmethanes in the corresponding reactions indicated that bulky triarylmethanes, once formed inside the crystalline framework, have strong diffusional limitations to get out of the zeolite cavities and can undergo subsequent protolytic cleavage. A decrease in the activity of the zeolite to catalyze hydride transfer reactions lead to a decrease on the diphenylmethane yield. Finally, diphenylmethane appears as a primary product indicating that a series of consecutive reactions such as the formation of diarylcarbinols followed by protonation, water elimination, and hydride abstraction are taking place inside the pores of the zeolite before the real primary product comes out from the zeolite.

INTRODUCTION

Modified zeolites are finding new applications as heterogeneous acid catalysts for organic reactions in the liquid phase and at moderate temperatures (*1*). This is due not only to the advantages associated to the use of solid acids, i.e., easy work-up and regeneration, non-contaminant wastes, etc., but also to the possibility for controlling the catalytic properties of the active sites by means of variations in their crystalline structure, ion exchange, framework Si/Al ratio, and other structural features (*2*).

Recently we studied the condensation of formaldehyde with benzene in the presence of a series of acid Y zeolites (*3*), and it was concluded that only strong acid sites, those with $pK_a < 0$, were able to catalyze this reaction, increasing the lifetime of the catalyst when increasing the framework Si/Al ratio of the solid. Thus, good conversions and selectivities for the formation of diphenylmethane were obtained with a USY zeolite with a unit cell size of 24.51 Å. Since protonation of the carbonyl group is the first common step in acid-catalyzed aldehyde and ketone condensations (4) we considered that these conclusions should be valid for other analogous transformations. These types of aromatic alkylations are of practical importance since large scale processes such as the bisphenol A preparation, aniline–formaldehyde oligomerization, and phenol–formaldehyde polymerization are examples of this type of reaction (*5*). Moreover, well-known procedures for the preparation of heterocyclic compounds involve the intramolecular cyclocondensation of an aromatic carbonyl compound as the final step (*6*).

In the present work we have extended the scope of the formaldehyde alkylations

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[1] To whom correspondence should be addressed.

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of benzene catalyzed by acid zeolites, by performing the reaction of four aldehydes with five benzene derivatives in the presence of a series of USY zeolites ranging from 2.451 to 2.430 nm of unit cell size. The aim is to know what products are formed and their distribution when the aromatic ring allows positional isomers, relating the results to the structure of the reagents and determining the role played by the zeolite catalysts.

EXPERIMENTAL

Catalysts

The USY-1 zeolite was prepared stirring a commercial NaY sample (SK-40, Union Carbide) with a 0.25 *M* aqueous solution of ammonium acetate using a solid–liquid weight ratio of 1 : 4 at 25°C for 30 min. The exchanged zeolite was dried at 110°C for 6 h and deep-bed calcined at 550°C for 3 h. This partially exchanged NaHY was submitted to two additional exchange-calcination treatments first with a 0.40 solution and then with a 0.60 *M* solution of ammonium acetate following the above experimental procedure.

Chemical analysis determined that the Na_2O content of the resulting USY-1 was less than 2% by weight of the initial composition. The crystallinity was 85% of the initial NaY, while the unit cell size measured by XRD, following the ASTM D-3942-8 procedure, was 24.41 Å, which according to the Fitchner–Smittler equation (*7*) corresponds to 19 Al per unit cell.

Dealuminated HY-200, HY-250, HY-300, HY-350, and HY-450, were obtained by treating the commercial NaY material with $SiCl_4$ at the temperature indicated by the number, following the method described by Beyer and Belenkaya (*8*). Finally the resulting zeolites were submitted to two consecutive exchange calcination processes using a 0.40 and 0.60 *M* aqueous solution of ammonium acetate working as it has been described for USY-1. The Na_2O content of the resultant samples was less than 2 wt% of the Na_2O content of the starting material. The unit cell sizes, and the number of framework Al per unit cell are given in Table 1. BET surface areas and pore-size distribution measured by N_2 adsorption and desorption are also given in Table 1.

Reaction Procedures

Zeolite-catalyzed reactions. Activation of the catalysts was performed *in situ* by heating the solid (1.00 g) at 150°C under vacuum (1 Torr approximately) for 3 h. After this, the system was left at room temperature and then a solution of nitrobenzene (100 mg) as internal standard and the corresponding aldehyde (200 mg) in the appropriate aromatic compound (50 ml) as solvent was poured onto the activated catalyst. The resulting suspension was stirred magnetically at the solvent reflux temperature for 17 h. At the end of the reaction the catalyst was filtered, washed with dichloromethane, the organic solution concentrated in vacuum, and the residue weighed and analyzed by gas chromatography–mass spectrometry (GC–MS) using a Hewlett-Packard 5988A spectrometer provided with a 25-m capillary column of cross-linked 5% phenylmethylsilicone. The ^1H NMR analysis was carried out with a 60-MHz Varian 360 EM spectrometer in tetrachloromethane as solvent and TMS as internal standard. The zeolite was submitted to continuous solid–liquid extraction with dichloromethane using micro-Soxhlet equipment. After removal of the solvent, the residue was also weighed and analyzed by GC–MS and ^1H NMR spectroscopy. In all cases the recovered material accounted for more than 90% of the starting aldehyde.

Isolation of pure isomeric compounds was accomplished by high performance liquid chromatography (HPLC) using an isocratic Waters apparatus provided with a semipreparative Microporasil column and mixtures of hexane–ethyl acetate as eluent. ^1H NMR spectra of 200 MHz were recorded in a Varian model Geminis using deuterated trichloromethane as solvent and TMS as internal standard.

The chemical structures and their corresponding numbers of all the products obtained in this study are presented in Fig. 1.

TABLE 1

Physicochemical Characteristics of the Zeolite Catalysts

Zeolite	Unit cell size (Å)	Al per unit cell	Crystallinity (SK-40 = 100%)	S_{BET} $m^2 \cdot g^{-1}$	Pore volume (10–30 Å)	Na_2O (wt%)
USY-1	24.41	19	85	576	0.05	0.07
HY-200	24.56	37	100	516	0.01	0.08
HY-250	24.50	30	100	581	0.01	0.07
HY-300	24.47	27	100	623	0.02	0.07
HY-350	24.43	22	95	600	0.03	0.05
HY-450	24.25	1.9	95	581	0.05	0.04

The letter *R* refers to the substituent on the aromatic ring and can represent a methyl, chloride, methoxy, or hydrogen for the series of products named *a*, *b*, *c*, and *d*, respectively.

$AlCl_3$-catalyzed reactions. Aluminum chloride (250 mg, 1.9 mmol) was added to a solution of the corresponding aldehyde (200 mg) in the aromatic compound (50 ml) and the resulting mixture stirred magnetically at 50°C for 1 h. Then, the organic layer was thoroughly washed, first with concentrated hydrochloric acid and finally with water. After it was dried over anhydrous Na_2SO_4, the reaction mixture was concentrated in vacuum and the residue analyzed by GC–MS.

RESULTS AND DISCUSSION

Assignment of the reaction product structures (see Fig. 1) were based on the NMR spectra together with the observation in the GC–MS analysis of intense peaks for the corresponding molecular ions, and the pattern for the aromatic protons in the ^1H NMR and the out-of-plane C–H bending vibrations of the aromatic rings in the region between 900 and 700 cm^{-1} in the IR (9). The reactions proceeded cleanly and in all cases the unidentified by-products accounted for less than 5% of the total weight. The results attained for the condensation of aliphatic aldehydes with benzene derivatives on USY-1 zeolite are summarized in Table 2 and are expressed as the molar ratio product-to-initial limiting reagent in percentages.

In a first stage, the alkylation by formaldehyde of slightly activated or deactivated monosubstituted benzene derivatives, was carried out using USY-1 zeolite or $AlCl_3$ as catalyst. As expected, a mixture of three diarylmethanes **1–3** was obtained in each case, corresponding to the *ortho–ortho'* (**1a–c**), *ortho–para'* (**2a–c**), and *para–para'* (**3a–c**) positional isomers. The measured average **1**:**2**:**3** using the USY-1 catalyst was 0.44/1.25/1, while the same ratio for the $AlCl_3$ catalyst was 0.80/1.34/1. A comparison indicates that while the relative percentage of the *ortho–para'/para–para'* isomers is similar for both catalysts, USY-1 clearly inhibits the *ortho–ortho'* product (Table 3).

As the formation of diarylmethanes involves two consecutive electrophilic attacks to an aromatic ring with an *ortho/para* directing substituent, a likely explanation for the above finding would be that the *ortho*-to-*para* ratio for the first alkylation is almost the same for both catalysts, but it is different for the second one, where the zeolite would be more selective against *ortho–ortho* substitution than $AlCl_3$. This fact would indicate that the crystalline structure of the zeolite does not exert significant steric constraint in the formation of intermediate benzylic alcohols and the geometrical limitation imposed by the zeolite only takes place in the second arylation. This rationalization is consistent with the remarkable increase in the size of the different species involved in the mechanism.

In order to confirm the role played by the

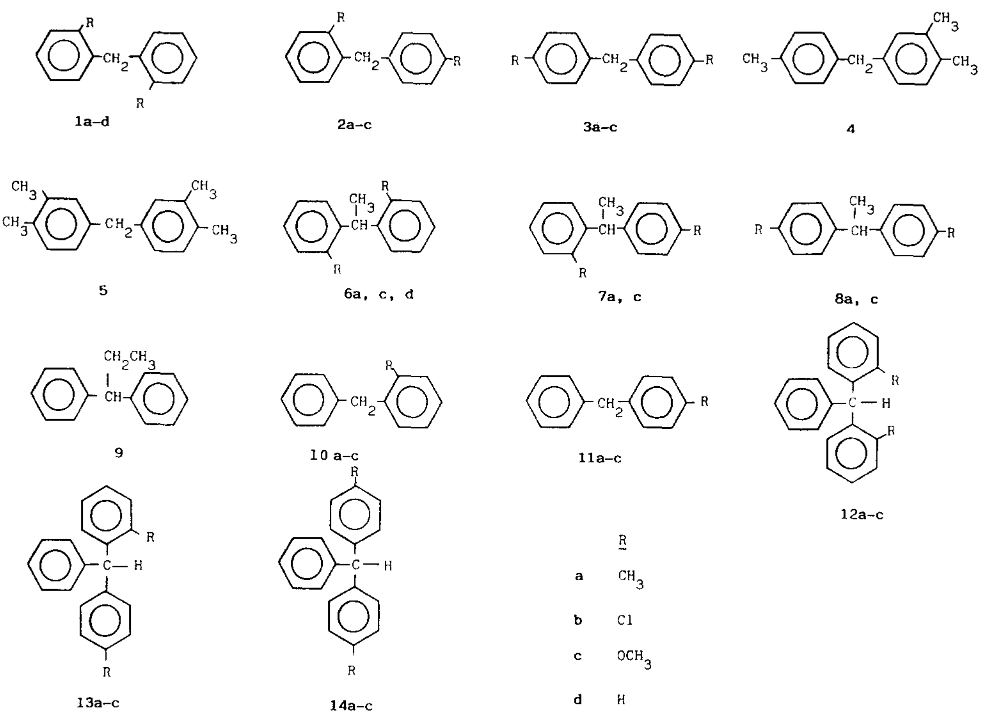


FIG. 1. Chemical species referred to in this paper.

crystalline structure of the USY-1 disfavoring the *ortho–ortho'* isomer, an alternative set of experiments using as catalyst a 1 : 1 w/w mixture of $AlCl_3$ and amorphous aluminosilicate (25 wt% of Al_2O_3 content) was performed, and the results were very similar to those reported in Table 3 using $AlCl_3$ alone. This fact supports our conclusion that the structure of the zeolite governs the selectivity of the *ortho–para* conversion.

Also in agreement with the size of the

TABLE 2

Results of the Reaction of Aliphatic Aldehydes with Benzene Derivatives in the Presence of USY-1

Carbonyl compound	Arene	Total product yield	Products (yield, %)
CH_2O	$PhCH_3$	72	**1a** (14), **2a** (31), **3a** (27)
	PhCl	38	**1b** (5), **2b** (19), **3b** (14)
	$PhOCH_3$	85	**1c** (16), **2c** (44), **3c** (25)
	o-$(CH_3)_2C_6H_4$	75	**4** (12), **5** (63)
CH_3CHO	PhH	6	**6d** (6)
	$PhCH_3$	38	**6a** (2), **7a** (15), **8a** (21)
	PhCl	<1	— — —
	$PhOCH_3$	48	**1c** (3), **2c** (5), **3c** (9), **6c** (3), **7c** (7), **8c** (21)
CH_3CH_2CHO	PhH	5	**9** (5)

TABLE 3

Reaction of Aliphatic Aldehydes with Benzene Derivatives: Comparison $AlCl_3$ vs USY-1 Catalysis

Carbonyl compound	Arene	Products oo′ : op′ : pp′	Product ratio over catalysts	
			$AlCl_3$	USY-1
CH_2O	$PhCH_3$	**1a** : **2a** : **3a**	0.8 : 1.25 : 1	0.52 : 1.15 : 1
	PhCl	**1b** : **2b** : **3b**	0.8 : 1.42 : 1	0.36 : 1.36 : 1
CH_3CHO	$PhCH_3$	**6a** : **7a** : **8a**	0.18 : 0.45 : 1	0.10 : 0.71 : 1

products involved, a comparatively remarkable selectivity to the *para*-substitution in the presence of USY-1 was observed (Table 2) when formaldehyde reacted with 1,2-dimethylbenzene to yield the compounds **4** and **5** or when acetaldehyde was used as carbonylic reagent to give the *ortho–ortho′*, *ortho–para′*, and *para–para′* isomers of the 1,1-diarylethanes (products **6–8**). The rather low conversions attained for the latter aldehyde, which did not react appreciably with the deactivated chlorobenzene, can be due to the general well-known decrease of the carbonyl reactivity as consequence of the substitution of H by methyl on this group (*10*). In this context, as could be expected taking into account the chemical behavior of both aliphatic aldehydes, the result of the condensation of propionaldehyde with benzene is similar to that found for the acetaldehyde (Table 2), giving additional support to our proposal.

On the other hand, benzaldehyde reacts with benzene and its monosubstituted derivatives in the presence of USY-1 to afford complex mixtures of diaryl **1–3, 10, 11** and triarylmethanes **12–14.** A series of experiments were carried out using as catalyst a series of Y zeolites with several framework Si-to-Al ratios to afford mixtures of diphenyl and triphenylmethane in different proportions depending on the Al content. The systems studied and their results are summarized in Table 4.

Two conclusions can be drawn from this table. First, the lower conversions achieved with benzaldehyde compared with formaldehyde correspond to the decrease in reactivity of the carbonyl group due to the conjugation with an aromatic ring. Second, the greater *para*-substitution selectivity for the triarylmethanes is probably due to the increase of the steric hindrance introduced by the phenyl ring in **12–14** compared with an hydrogen atom in **1–3.**

Reaction Mechanism

Due to the simplicity of the product distribution, we have chosen, as a model reaction, the condensation of benzaldehyde with benzene. In this case, the products obtained were diphenyl **1d** and triphenylmethane **12d** (Table 4). When the yields obtained at different reaction times were plotted (Fig. 2), it appears that diphenylmethane is a primary plus secondary product, while triphenylmethane is a primary and unstable product.

In the case of a non-zeolitic catalyst, such as BF_3, it has been reported (*11*) that the condensation of benzaldehyde with aromatic compounds does not give triarylmethanes, but diarylmethanes with minor amounts of benzoic acid, together with substantial quantities of heavy tars.

The proposed mechanism involving the intermediacy of benzyl benzoates generated by disproportionation of aldehydes could not fully justify all their experimental data (*11*). Moreover, in our case, using the USY-1 zeolite as catalyst, all attempts to detect benzoic derivatives were unsuccessful.

On the other hand, the accepted general mechanism for analogous carbonyl condensations with arenes involves a usually nonisolable benzylic alcohol formed by initial oxygen protonation on the C=O group and

TABLE 4

Results of the Reaction of Benzaldehyde with Benzene Derivatives in the Presence of HY Zeolites

Arene	Catalyst	Si/Al	Total product yield	Products (yield, %)	Remarks
PhH	USY-1	8.6	12	**1d** (4.0), **12d** (8.0)	Ratio **12d** to **1d** 2.0
	HY-200	4.2	6.2	**1d** (2.0), **12d** (4.2)	2.1
	HY-250	5.4	15.9	**1d** (3.4), **12d** (12.5)	3.7
	HY-300	6.2	7.6	**1d** (1.1), **12d** (6.5)	5.9
	HY-350	7.7	6.5	**1d** (1.0), **12d** (5.5)	5.5
	HY-450	99.4	5.3	**1d** (0.8), **12d** (4.5)	5.6
$PhCH_3$	USY-1		69	**10a** (2.5). **11a** (3.5), **1a** (3.5), **2a** (4.5), **3a** (2.5), **12a** (20.0), **13a** (22.0), **14a** (10.5)	**1d** and one isomer of tritolymethane were detected.
PhCl	USY-1		18.7	**10b** (2.0), **11b** (2.5), **12b** (1.0), **13b** (5.2), **14b** (8.0).	
$PhOCH_3$	USY-1		70	**10c** (10.0), **11c** (11.0), **1c** (5.0), **2c** (5.0), **3c** (19.0), **13c** (9.0), **14c** (11.0)	

subsequent electrophilic attack of the aromatic nucleus. This reactive intermediate would undergo further protonation and water elimination to generate a stabilized carbocation which would react with a second arene molecule. This mechanism is represented in Scheme 1, for the particular case considered here, and would justify the formation of the isomeric triarylmethanes **12–14** as primary products if a fast protonation of the benzylic alcohol is assumed (the asterisk denotes *ortho-* and *para*-isomers). Two alternative processes can be envisaged to explain the observed mixtures of diarylmethanes (Scheme 2, the asterisk denotes *ortho-* and *para*-isomers). Both processes have in common a step involving a hydride transfer to a diarylmethyl cation, being different in the actual precursor of these species, the non-isolated diarylcarbinol by protonation and water elimination (route **i**) or the triphenylmethanes by protolytic cleavage (routes **ii** and **iii**).

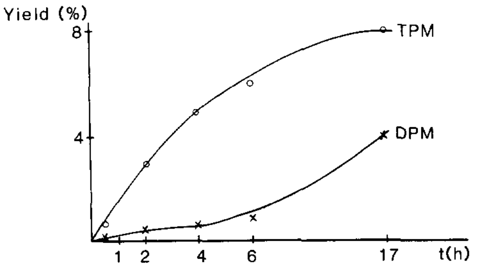
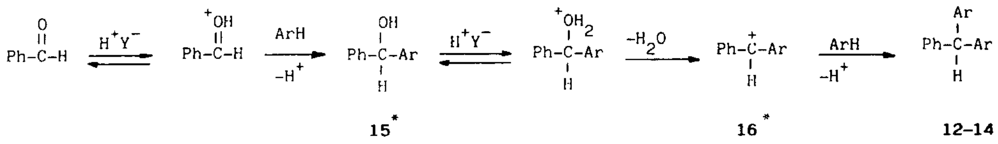


FIG. 2. Yield (%) of diphenyl **1d** (×) and triphenylmethane **12d** (O) versus the reaction time (*h*) for the condensation of benzaldehyde with benzene in the presence of USY-1.

Formation of diarylmethanes by protolytic cleavage of triarylmethanes could explain the secondary character of the diarylmethane fraction, as well as the unstable character of the triarylmethane fraction.

The diarylmethane product distribution for the condensation with toluene and anisole in Table 4 provides strong support that the operating mechanism is the cleavage of triarylmethanes leading to the ditolyl and dianisyl derivatives (pathway **iii** in Scheme 2), unless we assume an important degree of improbable migration of methyl and me-



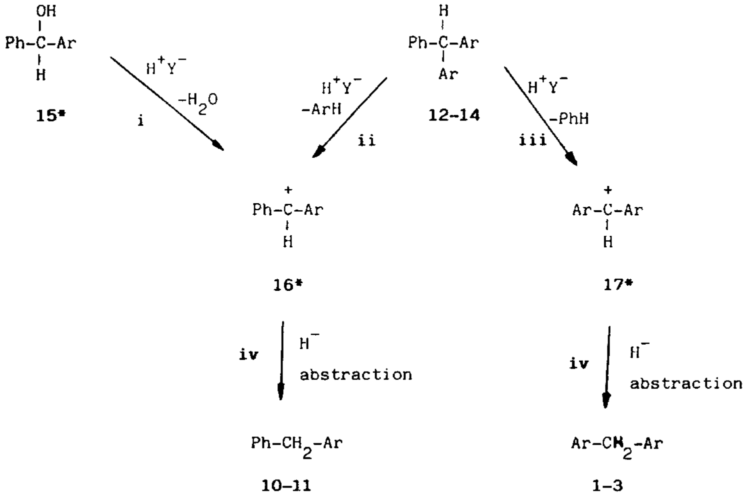
* ortho and para isomers

SCHEME 1.- Mechanism of formation of triarylmethanes

SCHEME 1

thoxy groups under the reaction conditions. Moreover, the relative stability of the possible diarylmethyl cation intermediates 16 and 17 will determine the relative rate of routes **ii** and **iii** and therefore we should expect a gradual change in the ratio of products **1–3** to **10, 11** as a function of the substituent ability to release or withdraw electron density on the aromatic nuclei in the series MeO, Me, and Cl, as observed (Table 4).

In order to get additional evidence on pathways **ii** and **iii** in Scheme 2 as well as the observation of diphenylmethane (**1d**), a solution of triphenylmethane (**12d**) in toluene was heated at 110°C in the presence of the USY-1 zeolite for 24 h. Under these conditions, only the starting material **12d** could be recovered, showing the strong limitations of the triarylmethane to diffuse inside the pores of the zeolite. The formation of diarylmethane from either route **ii** or **iii**, involves a hydride transfer step. If this is



*Ortho and para isomers

SCHEME 2.- Proposals for the formation of diarylmethanes

SCHEME 2

so, depending on the relative ability of the zeolite to catalyze the hydrogen transfer reactions, the ratio of tri- to diarylmethanes will be different. Indeed, when the reaction is carried out on USY zeolites with different framework Si/Al ratios (Table 4), it can be seen that the ratio of triphenylmethane to diphenylmethane increases when the Si/Al ratio increases. This is in agreement with the fact that the higher the framework Si/Al ratio of the zeolite, the lower its hydrogen transfer ability (*12*). Then, the contribution of diarylcarbinols **15** to the formation of **1d** may be explained assuming that hydride donors are present at the initial stages of the reaction. The diarylcarbinols can also act as a hydride donors, since the dismutation of benzylic alcohol to toluene and benzaldehyde over alumina at 250°C can be considered a related precedent (*13*). However, all our attempts to detect benzophenone in the course of the benzaldehyde reaction were unsuccessful. Therefore, the nature of hydride-donating species remains unknown at the present, although the high stability of cations generated from **15** and triarylmethanes by hydride transfer is obvious. These cations would be strongly adsorbed on the zeolite surface and not observed in the organic solution, and probably would act as a "hidden" source of successive hydride ions in its way to coke or to other unidentified polymeric materials. Coke formation will decrease with increase of the framework Si/Al ratio of the zeolite and, also from this point of view, the ratio of **12d** to **1d** products should increase with increase of the Si/Al ratio of the zeolite.

Finally, the occurrence of a small degree of methyl migration in the condensation of aldehydes with methylated benzenes in the presence of USY-1 (entries xylene in Table 2 and toluene in Table 4) was confirmed performing the reaction of diphenylmethane in toluene at 110°C for 17 h and observing the formation of *para*-benzyltoluene **11a** (4%). On the other hand, it is worth mentioning that for the reactions involving methoxy-substituted aromatic rings, no products arising from demethylation or methyl rearrangement could be detected.

CONCLUSIONS

In the present work we have shown that the condensation of aldehydes with benzene derivatives can be catalyzed by Y zeolites to give mixtures of the possible *ortho*- and *para*-substituted diarylalkanes. Comparison with the $AlCl_3$-catalyzed reaction shows that Y zeolite catalysts exert significant product shape selectivity only on the second arylation step. On the other hand, the influence of the structure of the aldehyde and the arene on the reactivity follows the general pattern known for carbonyl nucleophilic additions or electrophilic aromatic substitutions. A small degree of methyl transfer for the reactions in toluene or xylene has also been observed.

Finally, benzaldehyde reacts with benzene derivatives to yield mixtures of diaryl- and triphenylmethanes. While the latter can be expected to be formed, according to the condensation mechanism (Scheme 1), the former ones have been rationalized assuming hydride transfer to stabilized diarylmethyl cations, which would be generated both from the initial arylcarbinols **15** (route **i** in Scheme 2) and the tirarylmethanes **12–14** by protolytic cleavage (routes **ii** and **iii** in Scheme 2).

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