

First heterogeneously palladium catalysed α -arylation of diethyl malonate

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Abstract

Pd exchanged NaY zeolites ([Pd(0)]–, [Pd(II)]– and entrapped [Pd(NH₃)₄]) exhibit a good activity towards the α -arylation of carbonyl compounds using different *para*-substituted aryl bromides. Low Pd-concentrations (only 2 mol%) are required to observe interesting activity. The catalysts can easily be separated from the reaction mixture and reused without any loss in activity. For large-scale applications the alternative use of an insoluble base as K₂CO₃ seems to be promising. The electronic nature of the aryl halides plays a limited role concerning the rate of the reaction. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Heterogeneous catalytic α -arylation; Carbonyl derivatives; Zeolite supported palladium; Aryl halides

1. Introduction

The synthesis of α -aryl carbonyl compounds has received much attention during the last decades [1]. Numerous stoichiometric arylating reagents have been developed, but their interest remains limited since the production of each α -aryl carbonyl compound required the preparation of different reagents [2]. Recently, in order to overcome this situation, the homogeneous Pd-catalysed arylation of ketones has been developed, leading thus to a useful direct synthesis [3]. To our knowledge no reports concerning the use heterogeneous catalysts have appeared up to now.

While the use of homogeneous catalysts constitutes today an inestimable choice (high activity and selectivity, good comprehension of the reaction paths), these catalysts are connected with problems of separation, recovery and regeneration. For industrial applications these difficulties are of economic importance (costs of the catalysts and of the purification process). Such problems could be principally minimised by the use of heterogeneous catalysts.

We have previously shown that Pd supported in zeolites (Pd(0)–, Pd(II)– and Pd-complexes) are efficient heterogeneous catalysts for C–C coupling reactions between aryl halides and alkenes (Heck reaction) [4]. More recently we reported, for the first time, the heterogeneously Pd-catalysed direct synthesis of aryl amines from aryl halides [5]. Due to the similarities between these reactions with the reaction considered here [6], we decided to investigate the potential of Pd-loaded zeolites as heterogeneous catalysts for the α -arylation of carbonyl compounds.

We describe that Pd-loaded zeolites are active and selective heterogeneous catalysts for the direct arylation of carbonyl derivatives via an enolate.

2. Results and discussion

2.1. Preparation of the catalysts

[Pd(NH₃)₄]²⁺–, Pd(II)– and the Pd(0)–NaY zeolites were prepared according to the literature by an ion exchange procedure [7]. Using an aqueous solution of [Pd(NH₃)₄]Cl₂, a 1 wt% [Pd(NH₃)₄]-zeolite was obtained. Calcination under O₂ of exchanged [Pd(NH₃)₄]²⁺–NaY gave the Pd(II)–NaY zeolite and subsequent reduction under H₂ lead to the formation of the Pd(0)–NaY zeolite (see Section 4).

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Analogously, the $[\text{Pd}(\text{OAc})_2]$ loaded zeolite was prepared by immobilisation of the complex in the zeolite. Since the diameter of the zeolite channels is limited (for the Y zeolite: $\varnothing = 7.4 \text{ \AA}$) [8], molecular modelling calculations were performed in order to check whether the complexes can pass through the zeolite window. The results obtained using the MM2 augmented parameters provided with the CACHE™ software from Oxford Molecular Ltd were reported elsewhere [4b]. Experimentally, we found that a 0.7 wt% $[\text{Pd}(\text{OAc})_2]$ –NaY zeolite was obtained after an exchange period of 3 days from a THF solution. This catalyst was then characterised by MAS-NMR, which has shown that the $\text{Pd}(\text{OAc})_2$ complex immobilised into the zeolite supercage was intact and gave compatible ^1H and ^{13}C spectra with the solution NMR spectrum of the free Pd-complex [4b].

2.2. Tests of the catalytic activity

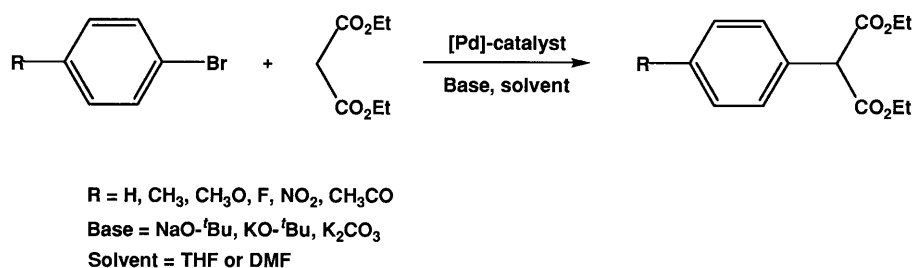
As a model reaction we chose the arylation of the diethyl malonate ($\text{EtO}_2\text{CCH}_2\text{CO}_2\text{Et}$) using aryl bromides (Scheme 1). Since this carbonyl derivative is symmetric, it limits the difficulties in the analysis of the

reaction products due to a mixture of regio-isomers. As was already mentioned in the literature [3d], results thus obtained can be extended to a larger family of carbonyl derivatives.

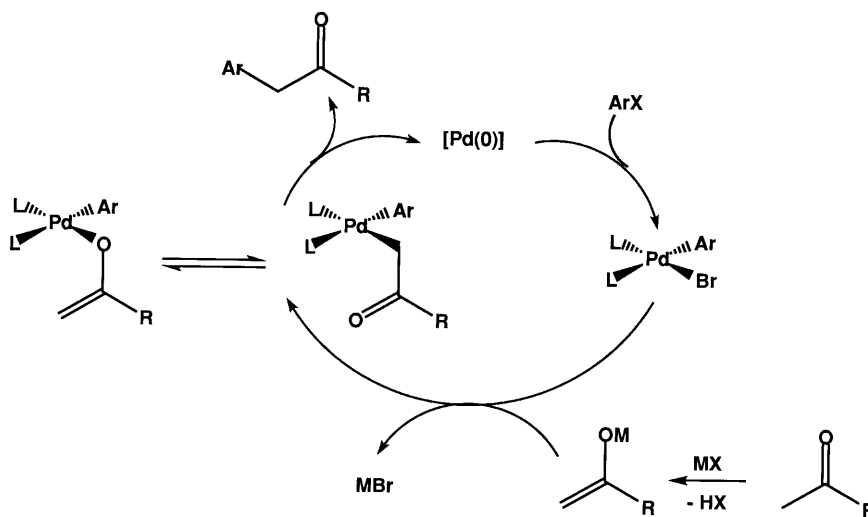
The choice of aryl bromides for the test of the catalytic activity was directed both by the real availability of these compounds and on the basis of the literature. Aryl bromides exist with a large variety of substituents on the aromatic ring, which can be used to test the tolerance of the reaction towards different functional groups. The variety of derivatives used represents a good basis for comparison of the heterogeneously (this paper) and the homogeneously catalysed arylation of carbonyl derivatives.

According to the literature, the Pd-catalysed arylation of carbonyl compounds can be described as a C–C coupling reaction between an aryl halide and an enolate (Scheme 2), which is produced in situ in presence of a base [3a].

One focus of our investigations of the new heterogeneously catalysed reaction, concerns the comparisons between homogeneous and heterogeneous systems. In order to obtain comparable data, we decided to run parallel experiments using as a ‘standard’ homogeneous



Scheme 1. Pd-catalysed α -arylation of diethylmalonate. Reaction conditions: 15 mmol aryl bromide, 10 mmol diethyl malonate, 20 mmol of base, 2 mol% $[\text{Pd}]$ -catalyst, 6 ml solvent, 110°C , 20 h.



Scheme 2. Proposed reaction pathway for the Pd-catalysed α -arylation of carbonyl derivatives ($\text{M} = \text{Na}, \text{K}, \text{Li}$).

Table 1

Results obtained for the arylation of diethyl malonate with *para*-bromotoluene (Scheme 1, R = CH₃) using 1 mol% Pd-catalyst as different [Pd]–NaY zeolite or as a standard homogeneous catalyst [Pd(OAc)₂]/PPh₃ (four equivalents)] in presence of NaOtBu in THF ^a

Entry	Catalyst	GLC yield	Isolated yield
1	Pd(0)–NaY	31	21
2	Pd(II)–NaY	41	32
3	[Pd(NH ₃) ₄]–NaY	51	38
4	[Pd(OAc) ₂]–NaY	41	29
5	[Pd(OAc) ₂]/PPh ₃ (four equivalents)	65	56

^a The GLC yields ($\Delta_{\text{rel}} \leq \pm 10\%$) and the isolated yields are given with regard to the diethyl malonate (carbonyl compound).

catalyst, the Pd(OAc)₂/PPh₃ system, although it is not known as the most active [3].

In the following we will describe and discuss the results obtained with respect to: the nature of the Pd-species immobilised into the NaY zeolite; the nature of the *para*-aryl substituent; the variation of the base and the solvent; and the recovery of the catalysts.

2.3. Influence of the nature of the Pd-species entrapped into the NaY zeolite

It has been previously described that the activity of the Pd-loaded zeolites used for C–C coupling reactions between aryl bromides and olefins was strongly dependent on the nature of the Pd-species entrapped in the cages at the beginning of the reaction [4,5]. Thus, a relation between the activity of the catalysts and the nature of the Pd-species was observed in terms of variation in Pd-dispersion attained during the preparation of the catalysts and in terms of different active Pd-species generated before and during the reaction [4]. Analogous to these works, we were interested to study such influence for the arylation of carbonyl compounds.

For these investigations we chose the reaction of diethyl malonate with the *para*-bromo toluene as arylating agent in presence of NaOtBu as base (Scheme 1, R = CH₃, Base = NaOtBu in THF).

Table 1 shows that the homogeneous catalyst is slightly more active than the heterogeneous catalysts used in this study. That can be a direct consequence of the reduced diffusion of the educts and products to and from the catalytic centres using zeolites as a support for heterogeneous catalysts.

As was previously described, the nature of the Pd-species entrapped into the zeolite at the beginning of the reaction has an influence onto the activity of the catalyst. Thus, as already observed, the [Pd(NH₃)₄]–NaY zeolite presents the highest activity [4b]. This can be correlated to a higher dispersion of the Pd-active

species that are created during the reaction, since the thermal treatments made for the preparation of the Pd(II)– and the Pd(0)–NaY catalysts tend to reduce the effective dispersion of the Pd-centres by an aggregation process.

The lower activity observed for the [Pd(OAc)₂]–NaY compared to the Pd(II)– or the [Pd(NH₃)₄]–NaY catalyst can be explained in terms of a reduced diffusion of the educts and/or the product into the zeolite channels due to the larger size of the Pd-complex compared to the other immobilised Pd-species. Alternatively, it could be the difficulty to create Pd-active species at the reaction temperature (110°C) as was described elsewhere [4b].

In addition to these experiments, we investigated whether the presence of Pd-species in zeolites was responsible for the activity. Thus, running an experiment in the presence of naked zeolite (Pd-free NaY) the formation of products resulting from the arylation of the diethyl malonate was never observed and in some cases degradation products (black mass) were obtained.

One should note that at the end of the reaction the remaining aryl bromide does not compensate the quantitative analysis (with regard to the starting *para*-bromo toluene) and that as side products of the reaction biphenyl derivatives were observed (typically 10–15% yields).

2.4. Influence of the *para*-aryl substituent

As for many organic reactions, it was interesting to study the generalisation of the heterogeneously Pd-catalysed arylation of carbonyl compounds, i.e. its tolerance towards a variety of functional groups. Thus, we studied the reaction between differently *para*-substituted aryl bromides and the diethyl malonate in the presence of NaOtBu as base in THF (Scheme 1).

The results reported in Table 2 show that the *para*-aryl substituent has a 'limited' effect on the reaction yield. As expected from the reaction mechanism proposed in Scheme 2, the limiting steps of the reaction should be (1) the oxidative addition of the arylating agent to the Pd(0)-centre, in which the nature of the *para*-aryl substituent plays a role and (2) the reductive elimination of the product in which, as already reported, the ligands present on the Pd(0)-centre are important. In the heterogeneous systems used in this study, the second limiting step can not be minimised. As for other Pd-catalysed C–C coupling reactions, the electronic nature of the aryl halide is crucial. Better results are obtained when the aryl halide presents in *para*-position an electron-withdrawing group (easiest oxidative addition). At this date, we could not explain the high yield obtained when the *para*-nitro bromobenzene is used as arylating agent since it could not be rationalised only in term of electronic effects. A possi-

Table 2

Results obtained for the arylation of diethyl malonate with different *para*-substituted aryl bromides using 1 mol% {[Pd(NH₃)₄]-NaY} as catalyst, or for the homogeneous runs, the system [Pd(OAc)₂]/PPh₃ (four equivalents)] in the presence of NaOrBu in THF (Scheme 1) ^a

Entry	R	Yield for heterogeneous catalyst	Yield for homogeneous catalyst
1	OCH ₃	57 (45)	62 (48)
2	CH ₃	51 (38)	65 (56)
3	H	47 (41)	58 (50)
4	F	64 (50)	72 (60)
5	CH ₃ CO	70 (62)	71 (64)
6	NO ₂	98 (84)	96 (78)

^a The GLC yields ($\Delta_{\text{rel}} \leq \pm 10\%$) and the isolated yields (in parenthesis) are given with regard to the diethyl malonate (carbonyl compound).

Table 3

Results obtained for the arylation of diethyl malonate with *para*-bromotoluene (Scheme 1, R = CH₃) using 1 mol% Pd-catalyst as [Pd]-NaY zeolite or [Pd(OAc)₂]/PPh₃ (four equivalents)] in the presence of different bases in a given solvent ^a

Entry	Base	Solvent	GLC yield for heterogeneous catalyst	GLC yield for homogeneous catalyst
1	NaOrBu	THF	41	65
2	NaOrBu	DMF	45	67
3	KOrBu	THF	39	40
4	KOrBu	DMF	46	60
5	K ₂ CO ₃	THF	6	8
6	K ₂ CO ₃	DMF	24	32

^a The GLC yields ($\Delta_{\text{rel}} \leq \pm 10\%$) and the isolated yields are given with regard to the diethyl malonate (carbonyl compound).

ble explanation is that this compound, due to its highest polarity and its strong dipole moment, diffuses better into the zeolite.

2.5. Influence of the base and the solvent

As suggested by the reaction pathway (Scheme 2), the nature of the base could influence the formation of the intermediate enolate and thus influence the overall activity observed for the reaction. Thus, we were interested in a study concerning the effect of the base in a given solvent medium.

Table 3 shows that using a 'soluble base' as Na- or K-OrBu in THF or DMF at 110°C only a little effect is observed. On the contrary, when the base is not soluble in the medium (as K₂CO₃ in THF), no or little product was formed. This could be partially minimised by using a more convenient medium such as DMF. This promising result could be enhanced by increasing the reaction temperature to 130°C, for which a reaction yield of 34.7% using the [Pd(NH₃)₄]-NaY was obtained.

These results are promising for industrial applications of this reaction, since the low solubility of the K₂CO₃ in DMF at standard temperature allows its separation easily from the reaction mixture together with the catalyst. Unfortunately, the increase of the reaction temperature to 140°C results only in the formation of undefined products (black mass) with a dramatic decrease of the reaction yields.

2.6. Recovery of the catalysts

An important point concerning the use of an heterogeneous catalyst is its lifetime, particularly for industrial applications.

After separation and washing, the heterogeneous catalysts were used for the same reactions (Scheme 1) under the same reaction conditions as for the initial run without any regeneration procedure. Table 4 shows that all the catalysts still showed a comparable activity as for fresh catalysts.

In addition to these experiments selected investigations concerning the leaching (residual activity of the supernatant solution after separation of the solid) were

Table 4

Results obtained for the arylation of diethyl malonate with *para*-bromotoluene (Scheme 1, R = CH₃) using recovered [Pd]-NaY catalysts in presence of NaOrBu in THF ^a

Entry	Catalyst	GLC yield first run	GLC yield second run
1	Pd(0)-NaY	31	33
2	Pd(II)-NaY	41	38
3	[Pd(NH ₃) ₄]-NaY	51	49
4	[Pd(OAc) ₂]-NaY	41	39

^a The GLC yields ($\Delta_{\text{rel}} \leq \pm 10\%$) are given with regard to diethyl malonate (carbonyl compound).

made. Using a specific filtration procedure (Whatman + nitrate-cellulose filters) for the separation of the solid catalyst, no activity at all was observed for most supernatant solutions. In the case of Pd(0)–NaY zeolites, a limited ‘leaching’ could be observed, but it can by far not explain the overall activity of the catalysts (see also recovery of the catalyst).

3. Conclusion

The heterogeneous [Pd]–NaY zeolite catalysts presented in this contribution show a good activity towards the arylation of diethyl malonate using differently *para*-substituted aryl bromides. While they do not rival with the best homogeneous catalysts developed recently principally by Hartwig et al. [3b,d,h] and Buchwald et al. [3a,e], they gave an alternative to the use of homogeneous catalysts for industrial applications where the cost of the catalysts are of importance. Remarkable is the comparatively low Pd-concentration (only 2 mol%) required to observe a reasonable activity. In addition, these catalysts can be easily separated from the reaction mixture (filtration) and reused without loss of activity.

As for other Pd-catalysed C–C coupling reactions, we found that the electronic effect of the aryl halide plays a role. Better results are observed when the arylating agent wear an electron-withdrawing group in the *para*-position. However, this effect was found to be limited since one of the limiting steps of the reaction is the reductive elimination of the product from the active Pd-centre.

In some cases, it was reported that the reaction tends to form some bis-arylated compounds. We never observed such derivatives using [Pd]–NaY catalysts, possibly due to the well-established ‘shape-selectivity’. However, in some cases we observed secondary products for the reaction, mainly some biphenyl derivatives.

Using an alternative base (K_2CO_3), promising results were obtained. Since one of the motivations for using heterogeneous catalysts instead of homogeneous analogues is the easier separation procedure, the use of the badly soluble K_2CO_3 as the base tends to achieve this objective. However, the results presented in this paper should be confirmed, and particularly the activity of the [Pd]–NaY/ K_2CO_3 /DMF (or an alternative solvent) system has to be enhanced.

Current investigations focus on the kinetic, the mechanism of the heterogeneously catalysed arylation of carbonyl compounds and the extension of this reaction to other industrially interesting substrates. New heterogeneous systems based on zeolites, carbon and metal oxide supports are under development. Thus, the grafting of Pd-complexes onto a surface or in a zeolite cages seems a to be a promising approach for combining the

advantages of the homogeneous catalysts with the advantages of the heterogeneous ones.

4. Experimental

All preparations, manipulations and reactions were carried out under argon, including the transfer of the catalysts to the reaction vessel. All glassware was base- and acid-washed and oven dried. The other chemicals (organic reagents) were deaerated by an argon flow before they were used. The THF used for the catalytic experiments was distilled under argon over sodium from purple benzophenone ketyl and stored over activated molecular sieves (4 Å) and the DMF (stored under nitrogen) was purchased from Sigma–Aldrich Chemicals as a Sure-Sealed Bottle. The NaY zeolite (LZ-Z-52) was purchased from Sigma–Aldrich Chemicals and the $PdCl_2$ used as precursor for the preparation of the catalyst was donated by Degussa-Huels Ag. The catalyst support was dried before use at 120°C for 48 h under 5×10^{-2} mmHg. All other chemicals were used as received. NMR spectra were recorded with a Bruker AM 400 spectrometer (1H -NMR were referenced to the residual protio-solvent: $CDCl_3$, $\delta = 7.25$ ppm; ^{13}C -NMR were referenced to the C-signal of the deuterio solvent: $CDCl_3$, $\delta = 77$ ppm). The palladium content determination of the catalysts was performed by AAS from a solution obtained by treatment of the catalysts with a mixture of HBf_4 , HNO_3 and HCl in a Teflon reactor at 180°C. Gas-liquid chromatograms were performed on a HP 6890 series chromatograph equipped with a FID detector and a HP-1 column (cross-linked methylsiloxane, 30 m $\times$ 0.25 mm $\times$ 0.25 μm film thickness) using He as carrier gas. Alternatively, a HP 5970 series chromatograph equipped with a selective mass-spectrometer detector HP 5970 and a BGB-1 column from SCP-Seitz GmbH (95% methylpolysiloxane + 5% phenylpolysiloxane, 25 m $\times$ 0.32 mm $\times$ 0.52 μm) using He as carrier gas was used.

4.1. Preparation of the catalysts

4.1.1. Procedure for the preparation of the $[Pd(NH_3)_4]$ –NaY

A 0.1 M ammoniac solution of $[Pd(NH_3)_4]Cl_2$, prepared from $PdCl_2$ and a commercial ammoniac solution (0.95 ml g^{-1} zeolite, corresponding approximately to 1% Pd in the final catalyst) was added drop wise to a suspension of the zeolite NaY in bidistilled water (100 ml g^{-1} zeolite). The mixture was stirred for 24 h at room temperature (r.t.) and the exchanged zeolite was filtered off and washed until no trace of chloride was detected in the filtrate ($AgNO_3$ test). Then the zeolite was allowed to dry at r.t. to give the entrapped $[Pd(NH_3)_4]^{2+}$ zeolite as a slightly yellow material. The AAS gave 1.0 ± 0.2 wt% Pd.

4.1.2. Procedure for the preparation of the [Pd(II)]–NaY

The Pd(II) exchanged zeolite was obtained by calcination of the [Pd(NH₃)₄]–NaY in a U-tube reactor under a pure oxygen flow (180 ml min^{−1}) using a heating rate of 2 K min^{−1} from r.t. to 500°C. The temperature was maintained at 500°C for 30 min and the reactor was cooled to r.t. under a flow of argon to give the Pd(II) zeolite as a tabac-coloured powder. The AAS gave 1.0 ± 0.2 wt% Pd.

4.1.3. Procedure for the preparation of the [Pd(II)]–NaY

The Pd(0) exchanged zeolite was obtained by reduction of the [Pd(II)]–NaY in a U-tube reactor under a pure hydrogen flow (70 ml min^{−1}) using a heating rate of 8 K min^{−1} from r.t. to 350°C. The temperature was maintained at 350°C for 15 min and the reactor was cooled to r.t. under a flow of argon to give the Pd(0) zeolite as a black powder. The AAS gave 1.0 ± 0.2 wt% Pd.

4.1.4. Procedure for the preparation of the [Pd(OAc)₂]–NaY

A solution of the Pd(OAc)₂ (110.2 mg, 0.47 mmol, corresponding approximately to 1% Pd in the final catalyst) in THF was added drop wise to a suspension of the zeolite NaY (4.95 g) in THF (20 ml g^{−1} zeolite). The mixture was stirred for 3 days at r.t. and the [Pd(OAc)₂] loaded zeolite was filtered off and washed with THF until no trace of non-immobilised complex was detected in the filtrate. Then the zeolite was allowed to dry at r.t. to give the entrapped [Pd(OAc)₂] zeolite as a slightly brown material. The AAS gave 0.7 ± 0.2 wt% Pd.

MAS-NMR: ¹H-NMR, ppm: 2.10 (CH₃CO).

MAS-NMR: ¹³C-NMR, ppm: 186,84 (CH₃CO); 23.04 (CH₃CO).

4.2. Test of the catalytic activity

Catalytic reactions were carried out in pressure tubes under argon. The Pd-catalysts were transferred under Ar. The qualitative and quantitative analyses of the reactants and the products were made by GLC. Conversion and selectivity are represented by GLC yields (= relative area of GLC signals referred to an internal standard calibrated to the corresponding pure compound, Δ_{rel} = ± 10%).

4.2.1. General procedure for the first run and the recycling of the catalysts

A total of 15 mmol of aryl bromide, 10 mmol of diethyl malonate, 20 mmol of base and 2 mol% of Pd (as heterogeneous catalyst, the amount in grams of catalyst depending on the Pd loading) were introduced

in a pressure tube under argon. A total of 6 ml of dry solvent previously deaerated was added and the mixture was further deaerated by an argon flow for 5 min. The reactor was then placed in a pre-heated oil bath at 110°C for 20 h with vigorous stirring and then cooled to r.t. before the reaction mixture was analysed by GLC.

For the recycling studies, a catalyst issue from a first run was used. After separation of the reaction mixture, it was washed with toluene and CH₂Cl₂ in order to remove all adsorbed organic substrates and dried at r.t.

4.3. GLC analysis

A homogeneous 3-ml sample of the reaction mixture was sampled and quenched with 5 ml of water in a test tube. A total of 3 ml of CH₂Cl₂ was added and the layers were shortly but vigorously mixed before the organic layer was separated. It was dried over MgSO₄ and filtered through a cotton pad. The resulting dry organic layer was then analysed by GLC or GLC-MS. GLC-rate program: AS 100 constant-pressure (130 KPa): 2 min at 100°C, heating at 15°C min^{−1} up to 170°C, 2 min at 170°C, heating at 35°C min^{−1} up to 240°C, 10 min at 240°C, heating at 50°C min^{−1} up to 270°C and 2 min at 270°C.

4.4. Purification of the malonate derivatives

When possible, the products of the arylation reactions were isolated and analysed by standard methods (¹H- and ¹³C-NMR). We give here the purification methods used, followed by the characterisation data.

After separation of the heterogeneous catalyst, the reaction mixture was evaporated. The residue was dissolved in CH₂Cl₂ (50 ml) and washed with water (3 × 20 ml). The organic layer was then dried over activated MgSO₄ and evaporated. The residue was then purified by chromatography over silica gel (50 g SiO₂ g^{−1} organic mixture, SiO₂ Merck Type 7754 70–230 mesh, 60 Å) eluting with CH₂Cl₂ to give the malonate derivative. Additional chromatography on silica was realised in order to obtain a higher purity. The purity of the products was estimated by GLC to be ≥ 90%.

4.5. Characterisation of the malonate derivatives

4.5.1. Data for the 2-Phenyl-malonic acid diethyl ester (R = H), colourless oil

¹H-NMR, CDCl₃, 400.13 MHz: 7.39 (pseudo-d, ³J = 6.7 Hz, 2H, *m*-C₆H₅); 7.29 (m, 3H, *o*-C₆H₅ and *p*-C₆H₅); 4.64 (s, 1H, CH); 4.15 (q, 4H, ³J = 8.0 Hz, OCH₂CH₃); 1.19 (t, 6H, ³J = 8.0 Hz, OCH₂CH₃).

¹³C-NMR, CDCl₃, 100.62 MHz: 168.80 (C=O); 133.76 (*ipso*-C₆H₅-CH); 130.05 (*o*-C₆H₅-CH); 129.27 (*m*-C₆H₅-CH); 128.88 (*p*-C₆H₅-CH); 62.38 (CH₂OCO); 58.64 (CH); 14.67 (CH₃CH₂O).

4.5.2. Data for the 2-*p*-tolyl-malonic acid diethyl ester ($R = CH_3$), colourless oil

1H -NMR, $CDCl_3$, 400.13 MHz: 6.94 (br. m, 4H, C_6H_4); 4.64 (s, 1H, CH); 4.14 (q, 4H, $^3J = 8.0$ Hz, OCH_2CH_3); 2.32 (s, 3H, $C_6H_4CH_3$); 1.24 (t, 6H, $^3J = 8.0$ Hz, OCH_2CH_3).

^{13}C -NMR, $CDCl_3$, 100.62 MHz: 169.02 (C=O); 136.52 (*p*- C_6H_4 -CH); 132.21 (*ipso*- C_6H_4 -CH); 129.86 (*o*- C_6H_4 -CH); 129.65 (*m*- C_6H_4 -CH); 61.86 (CH_2OCO); 56.72 (CH); 21.6 ($CH_3C_6H_4$); 14.09 (CH_3CH_2O).

4.5.3. Data for 2-(4-methoxy-phenyl)-malonic acid diethyl ester ($R = CH_3O$), colourless oil

1H -NMR, $CDCl_3$, 400.13 MHz: 6.98 (d, $^3J = 7.1$ Hz, 2H, *o*- C_6H_4); 6.69 (d, $^3J = 7.1$ Hz, 2H, *m*- C_6H_4); 4.59 (s, 1H, CH); 4.36 (q, 4H, $^3J = 8.0$ Hz, OCH_2CH_3); 3.76 (s, 3H, CH_3O); 1.30 (t, 6H, $^3J = 8.0$ Hz, OCH_2CH_3).

^{13}C -NMR, $CDCl_3$, 100.62 MHz: 170.12 (C=O); 160.86 (*p*- C_6H_4 -CH); 132.21 (*ipso*- C_6H_4 -CH); 129.86 (*o*- C_6H_4 -CH); 117.76 (*m*- C_6H_5 -CH); 62.08 (CH_2OCO); 56.86 (CH); 55.29 (CH_3O); 14.11 (CH_3CH_2O).

4.5.4. Data for 2-(4-fluoro-phenyl)-malonic acid diethyl ester ($R = F$), colourless oil

1H -NMR, $CDCl_3$, 400.13 MHz: 7.04 (d, $^3J = 8.0$ Hz, 2H, *o*- C_6H_4); 6.89 (d, $^3J = 8.0$ Hz, 2H, *m*- C_6H_4); 4.51 (s, 1H, CH); 4.21 (q, 4H, $^3J = 8.0$ Hz, OCH_2CH_3); 1.29 (t, 6H, $^3J = 8.0$ Hz, OCH_2CH_3).

^{13}C -NMR, $CDCl_3$, 100.62 MHz: 171.24 (C=O); 160.92 (*p*- C_6H_4 -CH); 132.52 (*o*- C_6H_4 -CH); 131.63 (*ipso*- C_6H_4 -CH); 116.29 (*m*- C_6H_5 -CH); 61.28 (CH_2OCO); 57.92 (CH); 14.08 (CH_3CH_2O).

4.5.5. Data for 2-(4-nitro-phenyl)-malonic acid diethyl ester ($R = NO_2$), yellow viscous oil

1H -NMR, $CDCl_3$, 400.13 MHz: 8.15 (d, $^3J = 9.0$ Hz, 2H, *o*- C_6H_4); 7.41 (d, $^3J = 9.0$ Hz, 2H, *m*- C_6H_4); 4.58 (s, 1H, CH); 4.25 (q, 4H, $^3J = 8.0$ Hz, OCH_2CH_3); 1.32 (t, 6H, $^3J = 8.0$ Hz, OCH_2CH_3).

^{13}C -NMR, $CDCl_3$, 100.62 MHz: 172.04 (C=O); 147.22 (*p*- C_6H_4 -CH); 141.23 (*ipso*- C_6H_4 -CH); 130.82 (*o*- C_6H_4 -CH); 124.19 (*m*- C_6H_5 -CH); 61.68 (CH_2OCO); 58.22 (CH); 14.18 (CH_3CH_2O).

4.5.6. Data for 2-(4-acetyl-phenyl)-malonic acid diethyl ester ($R = CH_3CO$), pale yellow viscous oil

1H -NMR, $CDCl_3$, 400.13 MHz: 7.72 (d, $^3J = 8.1$ Hz, 2H, *m*- C_6H_4); 7.17 (d, $^3J = 8.1$ Hz, 2H, *o*- C_6H_4); 4.61 (s, 1H, CH); 4.28 (q, 4H, $^3J = 8.0$ Hz, OCH_2CH_3); 2.58 (s, 3H, CH_3CO); 1.28 (t, 6H, $^3J = 8.0$ Hz, OCH_2CH_3).

^{13}C -NMR, $CDCl_3$, 100.62 MHz: 196.58 (C=O- CH_3); 172.24 (C=O); 139.58 (*ipso*- C_6H_4 -CH); 136.39 (*p*- C_6H_4 -CH); 130.02 (*o*- C_6H_4 -CH); 129.09 (*m*- C_6H_5 -CH); 61.72 (CH_2OCO); 58.42 (CH); 22.76 (CH_3CO); 14.08 (CH_3CH_2O).

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