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Journal of Catalysis 226 (2004) 192–196
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

The use of Lewis acids in the synthesis of 5-arylhydantoins

Carlos Cativiela [a], José M. Fraile [a], José I. García [a], Gustavo Lafuente [a], José A. Mayoral [a,*], Rachid Tahir [a], Antonio Pallarés [b]

[a] *Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain*
[b] *DSM Deretil, E-04618 Villaricos, Almería, Spain*

Received 29 March 2004; revised 12 May 2004; accepted 21 May 2004

Abstract

Different Lewis acids are able to promote the Friedel–Crafts reaction between 5-bromohydantoin and aromatic compounds. In the case of phenol, mixtures of *ortho* and *para* isomers are always obtained, with $Mg(ClO_4)_2$ leading to the best selectivity. However, the best overall yield of 5-(hydroxyphenyl)hydantoin is obtained with $YbCl_3$. This method can be extended to other aromatic systems such as anisole and thiophene. These reactions give similar yields but proceed with total selectivity to 5-(4-methoxyphenyl)hydantoin and 5-(2-thiophenyl)hydantoin, respectively. The cationic exchange of Mg^{II} and Yb^{III} on anionic solid supports allows the preparation of very efficient heterogeneous catalysts for this reaction (productivity up to 600 mol of hydantoin per mole of Mg). These catalysts have practical advantages in that they can be recycled and reused.

Keywords: Lewis acids; Arylhydantoins

1. Introduction

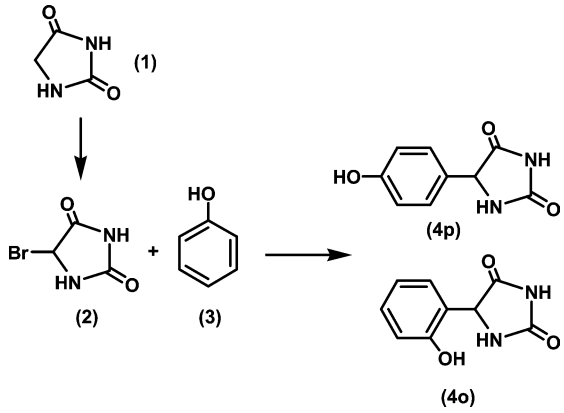
Racemic 5-arylhydantoins are important intermediates in the enzymatic production of (*R*)-2-arylglycines [1,2]. One of the most important examples is 5-(4-hydroxyphenyl)hydantoin (**4p**), which is used in the preparation of semisynthetic penicillins and cephalosporins [3,4].

In practice, 5-(4-hydroxyphenyl)hydantoin (**4p**) is obtained by the amidoalkylation of phenol with urea and glyoxylic acid [5,6]. This method suffers from two main drawbacks. First, a large excess of concentrated mineral acid is needed in order to attain high conversions. Secondly, a mixture of 5-(4-hydroxyphenyl)hydantoin (**4p**) and 5-(2-hydroxyphenyl)hydantoin (**4o**) is always obtained. We explored the use of heterogeneous acids in this reaction [7] and found that the solids did not improve on the conversion and selectivity obtained in solution, although recycling and reuse of the catalysts were possible. It is also possible to carry out the reaction in two steps. One synthetic route involves the reaction between glyoxylic acid and urea—leading to allantoin [8,9]—followed by the reaction with phenol [10]. Both steps require the use of a mineral acid, which can be replaced by solid acids [11]. However, neither the final yield nor the selectivity to 5-(4-hydroxyphenyl)hydantoin are better than those obtained in the direct synthesis. Another two-step route involves the synthesis of *p*-hydroxymandelic acid from glyoxylic acid and phenol and subsequent reaction with urea [12,13]. From our own experience [14], although this method may be an interesting alternative to the direct synthesis, the final yield of 5-(4-hydroxyphenyl)hydantoin is slightly lower and, once again, a large excess of an acid is required.

In view of these problems, we considered the possibility of using Lewis acids, rather than Brønsted acids, in catalytic amounts. In this approach it is necessary to use different starting materials and 5-halohydantoins were chosen as suitable substrates. We describe here the results of the reactions between 5-bromohydantoin (**2**) and phenol (**3**) (Scheme 1) with different homogeneous and heterogeneous Lewis acids. The extension of this methodology to include other aromatic compounds is also described.

* Corresponding author. Fax: +34 976762077
E-mail address: mayoral@unizar.es (J.A. Mayoral).

0021-9517/$ – see front matter
doi:10.1016/j.jcat.2004.05.021



Scheme 1.

2. Experimental

2.1. Synthesis and entrapment of 5-bromohydantoin (2)

Bromine (5.64 mL, 0.11 mol) was slowly added by syringe to a stirred solution of hydantoin (**1**, 10 g, 0.1 mol) in glacial acetic acid (or dioxane, 40 mL) at 100 °C under an inert atmosphere. On completion of the addition, the system was opened to allow the release of HBr and the solution was stirred for 45 min at the same temperature. The solution was cooled to 30 °C and triethyl phosphite (23.95 mL, 0.14 mol) was slowly added at such a rate that the temperature of the solution remained below 40–45 °C. The solution was stirred for 90 min and the solvent was removed under reduced pressure. Phosphonate **5** was crystallized from diethyl ether. Yield: 83%. ^{1}H NMR (d_6-dmso, δ ppm, J Hz): 10.91 (s, 1H), 8.41 (s, 1H), 4.75 (d, 1H, $J = 14.7$), 4.08 (m, 4H), 1.23 (t, 6H, $J = 7.0$).

When the bromination was carried out in acetonitrile under reflux, the only isolated product was the dimer **6**. ^{1}H NMR (d_6-dmso, δ ppm, J Hz): 11.18 (s, 1H), 11.01 (s, 1H), 8.19 (s, 1H), 5.78 (s, 1H), 3.95 (d, 1H, $J = 17$), 3.75 (d, 1H, $J = 17$). ^{13}C NMR (d_6-dmso, δ ppm): 170.8, 170.7, 156.7, 156.5, 63.0, 47.0.

2.2. Preparation of the catalysts

β-Zeolite (CP814E, surface area 680 $m^2\,g^{-1}$) in its ammonium form was purchased from Zeolyst.

The fluorosulfonic-type support (surface area 550 $m^2\,g^{-1}$, pore volume 0.75 $cm^3\,g^{-1}$, pore diameter 55 Å), represented as SiO_2–CF_2SO_3H and prepared from $(HO)_3Si(CH_2)_3$–$(CF_2)_2O(CF_2)_2SO_3K$ [15], was a generous gift from DuPont Research and Development. Prior to exchange, SiO_2–CF_2–SO_3H was transformed into its sodium form by passing a solution of 2 M NaCl through a column of the solid until neutral pH was obtained. The solid was then washed with deionized water and dried under vacuum at 150 °C overnight.

A solution of the metal salt [$YbCl_3$ or $Mg(ClO_4)_2$, 1 mmol] in methanol (10 mL) was added to the support (1 g) and the suspension was stirred at room temperature for 24 h. The solid was filtered, washed with methanol, and dried under vacuum overnight prior to use. Owing to the low cation content (see Table 3) the textural properties of the solids did not change to a great extent (surface areas 20–50 $m^2\,g^{-1}$ lower).

2.3. Synthesis of 5-arylhydantoins

Bromine (0.25 mL, 5.0 mmol) was slowly added (10 min) by syringe to a stirred solution of hydantoin (**1**, 500 mg, 5.0 mmol) in anhydrous dioxane (2 mL) at 100 °C under an inert atmosphere. On completion of the addition the solution was stirred for 40 min at the same temperature. The reaction mixture was cooled and the resulting solution was added to a mixture of the catalyst and aromatic compound (10.0 mmol). The reaction was stirred at 40 °C for the appropriate time (see Tables 1–3 for amounts of catalyst and reaction times). The catalyst was removed by filtration and the solvent was evaporated under reduced pressure. The products were crystallized from dichloromethane.

Table 1
Results obtained in the reaction between phenol and 5-bromohydantoin using homogeneous Lewis acids[a]

Entry	Catalyst (%)[b]	t (h)	% yield **4**[c]	**4p**/**4o**[d]
1	–	24	31	86/14
2	$Cu(OTf)_2$ (1%)	24	38	77/23
3	$ZnBr_2$ (1%)	24	45	82/18
4	$Mg(ClO_4)_2$ (1%)	24	66	85/15
5	$Mg(ClO_4)_2$ (2%)	4	82	85/15
6	$Yb(OTf)_3$ (1%)	24	63	73/27
7	$YbCl_3$ (1%)	21	86	76/24
8	$YbCl_3$ (2%)	4	84	78/22
9		16	93	76/24

[a] Reaction conditions: in situ preparation of 5-bromohydantoin from hydantoin (5 mmol) and bromine (0.3 mL) in dioxane (2 mL) at 100 °C; reaction with phenol (10 mmol) and catalyst at 40 °C.
[b] Amount of catalyst with respect to starting hydantoin.
[c] Isolated yield. Calculated from the starting hydantoin.
[d] Determined by ^{1}H NMR spectroscopy.

Table 2
Results obtained in the reaction between 5-bromohydantoin and different aromatics using homogeneous Lewis acids[a]

Entry	Aromatic	Metal salt (%)[b]	t (h)	% yield[c]
1	Anisole	$ZnBr_2$ (1%)	24	27
2		$ZnBr_2$ (5%)	24	45
3		$Mg(ClO_4)_2$ (5%)	21	67
4		$YbCl_3$ (5%)	16	60
5	Thiophene	$ZnBr_2$ (1%)	24	33
6		$ZnBr_2$ (5%)	21	60
7		$Mg(ClO_4)_2$ (5%)	20	71
8		$YbCl_3$ (5%)	16	75

[a] Reaction conditions: in situ preparation of 5-bromohydantoin from hydantoin (5 mmol) and bromine (0.3 mL) in dioxane (2 mL) at 100 °C; reaction with phenol (10 mmol) and catalyst at 40 °C.
[b] Amount of catalyst with respect to starting hydantoin.
[c] Isolated yield. Calculated from the starting hydantoin.

Table 3
Results obtained in the reaction between aromatic compounds and 5-bromohydantoin using heterogeneous Lewis acids[a]

Entry	Aromatic	Catalyst	Loading (mmol g^{-1})[b]	Run	t (h)	% yield[c] (productivity)	**4p**/**4o**[d]
1	Phenol	SiO_2–CF_2SO_3Mg	0.074	1	8	82 (554)	78/22
2				2	15	75 (507)	76/24
3				3	19	76 (514)	77/23
4		SiO_2–CF_2SO_3Yb	0.131	1	16	86 (328)	79/21
5				2	22	76 (290)	81/19
6		β-Mg	0.055	1	20	72 (655)	78/22
7				2	20	70 (636)	75/25
8		β-Yb	0.113	1	16	88 (389)	79/21
9				2	21	70 (310)	81/19
10	Anisole	β-Mg	0.055	1	15	38 (345)	–
11				2	24	28 (255)	–
12	Thiophene	β-Mg	0.055	1	15	34 (309)	–
13				2	21	26 (236)	–

[a] Reaction conditions: in situ preparation of 5-bromohydantoin from hydantoin (5 mmol) and bromine (0.3 mL) in dioxane (2 mL) at 100 °C; reaction with phenol (10 mmol) and catalyst (100 mg) at 40 °C.
[b] Determined by plasma emission spectroscopy.
[c] Isolated yield. Calculated from the starting hydantoin. Productivity is the number of molecules of product produced per catalytic site.
[d] Determined by ^{1}H NMR spectroscopy.

2.4. NMR spectra (d_6-dmso, δ ppm, J Hz)

5-(4-Hydroxyphenyl)hydantoin (**4p**): ^{1}H NMR: 10.69 (s, 1H), 9.51 (s, OH), 8.28 (s, 1H), 7.10 (d, 2H, $J = 8.5$), 6.76 (d, 2H, $J = 8.5$), 5.00 (s, 1H). ^{13}C NMR: 174.7, 157.4, 128.0, 126.3, 115.4, 60.9.

5-(2-Hydroxyphenyl)hydantoin (**4o**): ^{1}H NMR: 10.59 (s, 1H), 9.75 (s, OH), 7.98 (s, 1H), 7.12 (m, 2H), 6.78 (m, 2H), 5.11 (s, 1H). ^{13}C NMR: 175.1, 157.8, 155.9, 130.2, 129.6, 122.4, 118.9, 115.6, 58.5.

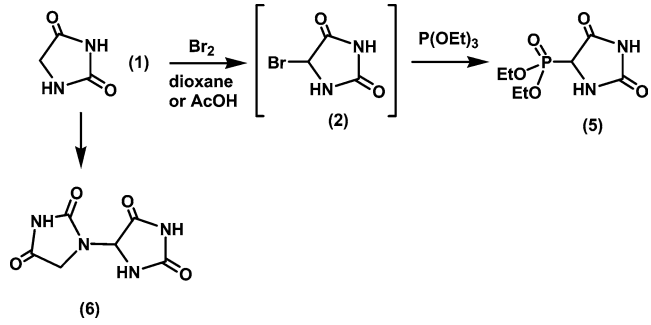
5-(4-Methoxyphenyl)hydantoin (**7**): ^{1}H NMR: 10.73 (s, 1H), 8.33 (s, 1H), 7.22 (d, 2H, $J = 8.5$), 6.95 (d, 2H, $J = 8.5$), 5.08 (s, 1H), 3.76 (s, 3H). ^{13}C NMR: 174.5, 159.2, 157.4, 127.9, 126.8, 114.0, 60.7, 55.1.

5-(2-Thiophenyl)hydantoin (**8**): ^{1}H NMR: 10.87 (s, 1H), 8.58 (s, 1H), 7.53 (d, 1H, $J = 5.1$), 7.11 (d, 1H, $J = 3.3$), 7.03 (dd, 1H, $J = 5.1, 3.3$), 5.47 (s, 1H). ^{13}C NMR: 173.1, 157.0, 138.8, 127.1, 126.1, 125.9, 57.4.

3. Results and discussion

3.1. Synthesis of 5-bromohydantoin (2)

5-Chloro- [16] and 5-bromohydantoin [17] had been described in the literature as intermediates in the synthesis of allantoin and 5-butoxyhydantoin, respectively. These compounds were prepared from hydantoin by reaction with $SOCl_2$ or Br_2. In both cases the 5-halohydantoins were described as unstable and they were preferably used without purification, a process also described in a more recent patent [18]. Given the problems encountered in the synthesis of 5-chlorohydantoin, 5-bromohydantoin was chosen as the starting material and it was prepared by reaction with bromine in different solvents (Scheme 2). Triethyl phosphite was added in order to entrap the 5-bromohydantoin as the



Scheme 2.

phosphonate (**5**) [19]. Dioxane and acetic acid were suitable solvents for this reaction and both led to high yields of phosphonate (> 80%). A high temperature is necessary for bromination and solvents with lower boiling points, such as THF, did not give any bromination at all. In some cases $ZnBr_2$ has been used as promoter in this bromination [18], but differences were not observed when dioxane or acetic acid were used. In acetonitrile the use of $ZnBr_2$ allows the isolation of a dimer (**6**), which indicates the role of the adjacent N–H bond. In order to assess the importance of this N–H bond, the bromination of N,N-dibenzylhydantoin was tested under the same conditions. The recovery of unaltered starting material clearly shows the importance of this functionality.

On the basis of the information outlined above, dioxane was chosen as the best solvent for bromination and the Friedel–Crafts reaction with phenol was carried out without isolation of 5-bromohydantoin.

3.2. Use of homogeneous Lewis acids in the synthesis of 5-arylhydantoins

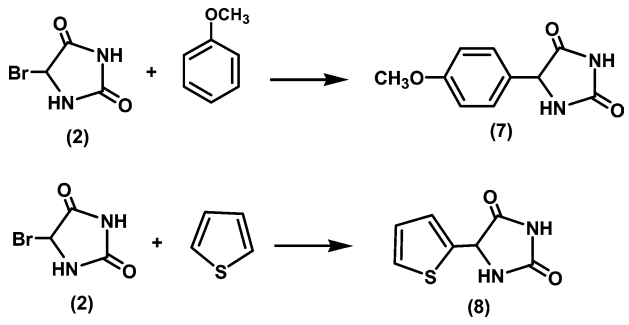
An excess (2 eq) of phenol and a Lewis acid catalyst were added to a solution of 5-bromohydantoin (Scheme 1).

The results of these reactions are gathered in Table 1. It has been reported [18] that this reaction takes place without a catalyst, but in our experience the yield is low (31%, entry 1). The use of $ZnBr_2$ improves the result (45%, entry 3) but the yield is still lower than that reported in the literature [18]. In view of this result, several different Lewis acids were tested. $Cu(OTf)_2$ (entry 2) was even less efficient than $ZnBr_2$. In contrast, $Mg(ClO_4)_2$ led to 66% yield after 24 h (entry 4). This result was improved by using a larger amount of catalyst (2%), which gave rise to 82% yield after only 4 h (entry 5).

Another interesting family of Lewis acids are the lanthanides [20,21], which allow a higher coordination number and, in many cases, are compatible with water. $Yb(OTf)_3$ (entry 6) showed an activity similar to that of $Mg(ClO_4)_2$ whereas $YbCl_3$ was clearly better (entry 7). In fact, the use of 2% of the latter catalyst gave 93% yield after 16 h (entry 9).

One of the most important aims from the point of view of the industrial synthesis of 5-(4-hydroxyphenyl)hydantoin is the *para*/*ortho* selectivity [7]. The Lewis acids promote the reaction, with *para*/*ortho* ratios in the range 73/27 to 85/15 and $Mg(ClO_4)_2$ is always more efficient than $YbCl_3$ with regard to selectivity. In this case the Lewis acids do not present the *ortho* preference shown in the synthesis of hydroxymandelic acid [22]. On the contrary these results are in agreement with the 82/18 ratio obtained in the synthesis from other cyclic intermediates, such as allantoin [11], promoted by Brønsted acids, and they are generally worse than the 86/14 ratio obtained in the direct synthesis [7]. In any case, these results represent a 70% yield of 5-(4-hydroxyphenyl)hydantoin with only 2% catalyst, a level close to the 77% obtained with 2.2 eq HCl (i.e., 220%) in solution.

The promising results described above encouraged us to extend this methodology to the reaction of 5-bromohydantoin with other aromatic compounds (Scheme 3). Anisole was the first choice given its similarity to phenol, albeit with a lower reactivity. The two best homogeneous catalysts, $Mg(ClO_4)_2$ and $YbCl_3$, together with $ZnBr_2$ were tested in this reaction (Table 2, entries 1–4). As expected, the yield was lower than in the case of phenol, up to 67% with $Mg(ClO_4)_2$, but with the important advantage that total *para* selectivity was achieved (within the experimental error of ^1H NMR spectroscopy). When the *para* isomer alone is taken into account, the yields obtained from phenol and anisole are very similar. This finding opens the way to the synthesis of pure 5-(4-hydroxyphenyl)hydantoin from O-protected phenols.



Scheme 3.

Thiophene was the other aromatic system tested (Table 2, entries 5–8) and the yields were slightly higher, up to 75% with $YbCl_3$. This increase in yield is consistent with the higher reactivity of thiophene and even $ZnBr_2$ is an efficient catalyst in this case. The reaction is also completely selective and in this case gives the 2-substituted thiophene. These results demonstrate the potential application of this method, given that the enzymatic kinetic resolution of this hydantoin would lead to enantiomerically pure α-amino-2-thiopheneacetic acid.

3.3. Use of heterogeneous Lewis acids in the synthesis of 5-(4-hydroxyphenyl)hydantoin (**4p**)

One way to improve this methodology concerns the ability to recycle the catalyst. With this aim in mind, Mg^{2+} and Yb^{3+} ions were exchanged onto anionic solid supports to obtain heterogeneous Lewis acids. Two different supports were investigated. First, a fluorosulfonic support with a rather high exchange capacity, prepared from silica and $(HO)_3Si(CH_2)_3(CF_2)_2O(CF_2)_2SO_3K$ [15]. This support has proven useful in the exchange of chiral bis(oxazoline)-copper complexes [23]. Secondly, a microporous β-zeolite was employed in an attempt to improve the *para*/*ortho* ratio through shape selectivity [24]. The results obtained in the synthesis of 5-arylhydantoins with these heterogeneous catalysts are gathered in Table 3.

The four heterogeneous Lewis acids were tested in the synthesis of 5-(4-hydroxyphenyl)hydantoin. A small amount of catalyst was used (100 mg) and this level represents very few Lewis acid sites (0.11 to 0.26% catalyst). Surprisingly, the reactions were very efficient, with yields of 5-(hydroxyphenyl)hydantoin in the range of 72 to 88% (entries 1, 4, 6, and 8). These yields are indicative of very high turnover numbers, leading to a site productivity (molecules formed per site) ranging from 328 in the case of SiO_2–CF_2SO_3Yb to 655 with β-Mg. The differences in the productivities of the two cations can be explained in terms of the different loading of each catalyst. This good behavior contrasts with the results obtained in the homogeneous phase, where 1–2% catalyst is necessary in order to obtain such reaction yields and, consequently, the productivities (38–86 molecules per site) are much lower. Although several factors can be proposed to explain this behavior, the effect of site isolation may be important in this case as it would allow the efficient use of all the metal atoms as Lewis acid sites.

Moreover, recycling of the heterogeneous catalysts is possible and only a slight reduction in the catalytic activity was observed with the recycled systems. Indeed, a third reaction was tried with SiO_2–CF_2SO_3Mg and this led to a total productivity after 3 runs of 1575 molecules per site,

an excellent result for a Friedel–Crafts reaction with rather complicated molecules.

The weight productivity in such processes is also an important factor and 16.9 g of 5-(4-hydroxyphenyl)hydantoin (22.4 g of the isomers mixture) was produced per gram of SiO_2–CF_2SO_3Mg after three reactions (under nonoptimized conditions). This productivity may be increased after further recycling experiments and opens the way to possible industrial applications.

In the case of zeolite catalysts, the activities and productivities are very similar to those obtained with the fluorosulfonic support. Unfortunately, a significant improvement in the *para*/*ortho* selectivity was not observed. Given its high productivity, zeolite β-Mg was chosen as the catalyst for the reaction between 5-bromohydantoin and the other two aromatic molecules (entries 10–13). It can be seen that the lower reactivities of anisole and thiophene reduce the isolated yields to 38 and 34%, respectively. It should be noted that these figures represent productivities of more than 300 molecules per site, again impressive for Friedel–Crafts alkylation reactions. The solids can be reused with only a slight reduction in activity, leading to overall productivities of 550–600 molecules per site.

3.4. Conclusions

5-Bromohydantoin has proven to be a valuable intermediate in the synthesis of 5-arylhydantoins. The reaction with aromatic systems is easily promoted by catalytic amounts of both homogeneous and heterogeneous Lewis acids. The heterogeneous catalysts not only give rise to very high productivities, but they can also be efficiently recycled with only a slight decrease in activity. Although the reaction with phenol leads to *para* + *ortho* mixtures, other aromatics allow the synthesis of only one isomer with total selectivity. This method opens the way to the synthesis of enantiomerically pure arylglycines by enzymatic kinetic resolution of the corresponding 5-arylhydantoins.

Acknowledgments

This work was made possible by the financial support of the Spanish M.C.Y.T. (project PPQ2000-0322-P4). R.T. is indebted to the M.C.Y.T. for a postdoctoral grant. We are indebted to Dr. Mark A. Harmer, from DuPont Research and development, for the generous gift of the fluorosulfonic support.

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