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Palladium-Catalyzed Synthesis of Substituted Hydantoins—A New Carbonylation Reaction for the Synthesis of Amino Acid Derivatives**

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Amino acids and their derivatives are unequivocally one of the most important classes of organic compounds. In addition to biochemical applications, amino acid derivatives are used as chemical feedstocks for industrial fine chemical synthesis.[1] Despite the well known "classical methods" such as the Strecker synthesis[2] and the highly selective procedures developed in the research groups of Schöllkopf,[3] Seebach,[4] Evans,[5] Williams[6] as well as recent developments,[7] a need for new, more efficient protocols for the preparation of amino acid derivatives remains. In the past, researchers focused exclusively on the asymmetric synthesis of amino acid derivatives, and successful procedures were judged accordingly. However, other important factors also need to be addressed. For example, the procedures need to be improved in terms of their atom economy.[8] This also applies to the asymmetric hydrogenation of acetamidoacrylates and acetamidocinnamates,[9] since the hydrogenation precursors are often expensive and difficult to prepare.[10]

Racemic imidazolidine-2,4-diones, generally called hydantoins,[11] are important building blocks for enantioselective amino acid synthesis because enantiomerically pure amino acids can be prepared from these by dynamic kinetic racemic resolution.[12] The practicability of this method was demonstrated on an industrial scale by Ajinomoto[13] and Kanegafuchi[14] for the production of D-*p*-hydroxyphenylglycine. Substituted hydantoins are also of pharmacological interest and are used, for example, for the treatment of epilepsy.[15] Since only atom economic procedures for the production of N-unsubstituted hydantoins are known (Bucherer – Bergs reaction,[16] amidoalkylation[17]), we set out to examine to what extent substituted hydantoins can be made directly from simple, inexpensive starting materials. We describe here a new one-pot synthesis of 5-, 3,5-, and 1,3,5-substituted hydantoins that is based on the carbonylation of aldehydes in the presence of urea derivatives.

In the context of our work on the carbonylation of aldehydes with amides (amidocarbonylation)[18] in the presence of a palladium catalyst,[19] we examined to what extent sulfonamide, urethanes and urea derivatives can be used as amide components. The conversion of cyclohexanecarbalde-

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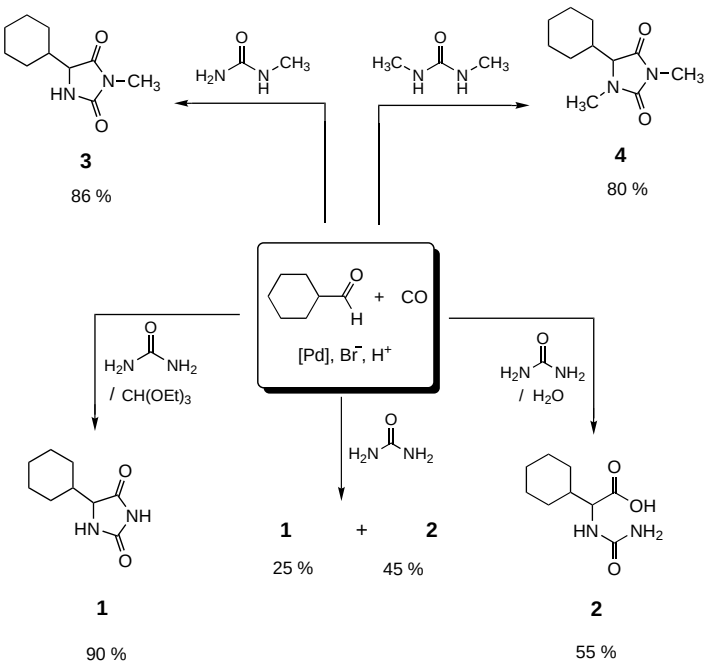
hyde with the respective amide component served as a model reaction. Although the reactions of sulfonamides and urethanes did not generate the desired product at 100 °C, the reaction with urea produced the 5-cyclohexylhydantoin **1** in 25% yield and *N*-carbamoyl-cyclohexylglycine **2** in 45% yield.[20] A 1:1 mixture of the starting materials in *N*-methylpyrrolidinone (NMP) as solvent in the presence of 0.5 mol% palladium(II) bromide/1 mol% PPh_3 was placed into a Parr autoclave and heated at 100 °C. After 12 h, the reaction mixture was allowed to come to ambient temperature, the volatile components were removed, and the products were isolated by simple extraction from water and ethyl acetate.

In order to demonstrate the utility of this reaction, the amidocarbonylation of cyclohexanecarbaldehyde was examined with a variety of substituted urea derivatives (Scheme 1; Table 1). Indeed, free urea gave very good selectivities (90%) for the hydantoin **1** when water-absorbing agents such as triethyl orthoformate or acetic anhydride were used. Interestingly,

Table 1. Palladium-catalyzed ureidocarbonylation with urea according to Equation (1).[a]

Entry	R^1	Additive [equiv]	Hydantoin product	Hydantoin yield [%][b]	*N*-Carbamoylic acid product	*N*-Carbamoylic acid yield [%][b]
1		–	**1**	25	**2**	45
2		$CH(OC_2H_5)_3$ [1.0]	**1**	90	**2**	n.b.
3		$(CH_3CO)_2O$ [1.0]	**1**	86	**2**	n.b.
4		H_2O [1.3]	**1**	20	**2**	55
5		–	**5**	5	**6**	35
6		$CH(OC_2H_5)_3$ [1.0]	**5**	64	**6**	n.b.

[a] Conditions: 25.0 mL solution (1.0 M in urea and aldehyde) in NMP, 0.25 mol% in situ prepared dibrombis(triphenylphosphane)palladium(II), 30 mol% LiBr, 1 mol% H_2SO_4, 60 bar carbon monoxide, 100 °C, 12 h. [b] Yield of isolated product; n.o. = not observed.

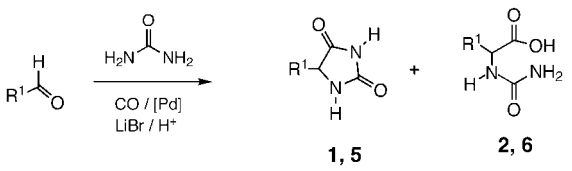


Scheme 1. Palladium-catalyzed carbonylation of cyclohexanecarbaldehyde with urea derivatives.

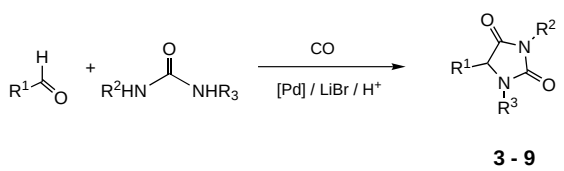
the free *N*-carbamoyl amino acid **2** can be prepared in good yields by simply combining one equivalent of water with the corresponding hydantoin.[21] The conversion of cyclohexanecarbaldehyde with monosubstituted dimethylurea occurs selectively. For example, at 80 °C the 5-cyclohexyl-3-methyl hydantoin **3** was obtained in very good yield (86%). The reaction with symmetrical dimethylurea led to the 5-cyclohexyl-1,3-dimethylhydantoin **4** in comparably high yield (80%). Prior to our work, 1,3,5-substituted hydantoins could only be prepared by multistep synthesis starting from the appropriate amino acids. In the first step, the nitrogen atom of the amino acid is monosubstituted by reductive alkylation. Acylation with isocyanate produces the appropriate carbamoyl, and subsequent base-promoted cyclization gives the hydantoin.[22]

The high selectivity of the 3,5-substituted hydantoins permits us to postulate a mechanism for this new ureidocarbonylation reaction. In agreement with the expected basicity of the different nitrogen atoms of monosubstituted urea derivatives, we assume that in a preequilibrium step, selective nucleophilic attack of the free NH_2 group on the carbonyl group takes place. An α-halogencarbamoyl species generated by nucleophilic substitution subsequently undergoes oxidative addition to the palladium(0) species. After CO insertion, the acylpalladium complex undergoes either an intramolecular reaction to give the hydantoin direcly, or first undergoes intermolecular attack of water to give the *N*-carbamoyl acid which subsequently cyclizes to the hydantoin.

The scope of this new multicomponent synthesis for hydantoins was demonstrated by the results summarized in Table 2. 3-Alkyl, 3-aryl or 3-benzyl substituted hydantoins were obtained in high selectivity from the corresponding monosubstituted urea derivatives (Eq. (2); Table 2, entries 1–5). When *N*,*N*′-disubstituted urea derivatives were em-



(1)



(2)

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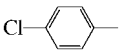
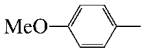
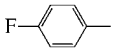
Table 2. Palladium-catalyzed ureidocarbonylation of aldehydes to substituted hydantoins according to Equation (2).[a]

Entry	R^1	R^2	R^3	Product	T [°C]	Yield [%][b]	TON
1		CH_3	H	**3**	80	86	344
2		CH_3	CH_3	**4**	80	80	320
3		C_2H_5	H	**7**	100	51	204
4			H	**8**	100	64	256
5			H	**9**	100	50	200
6[c]		CH_3	CH_3	**10**	100	80	80
7		C_2H_5	C_2H_5	**11**	100	89	356
8		CH_3	CH_3	**12**	120	61	244
9[d]	H			**13**	130	93	372
10	H	CH_3	CH_3	**14**	100	73	292
11		CH_3	CH_3	**15**	100	85	340
12		CH_3	CH_3	**16**	100	79	316
13[c]		CH_3	CH_3	**17**	100	70	70
14		CH_3	CH_3	**18**	100	44	176
15		CH_3	CH_3	**19**	100	39	156

[a] All conditions except the reaction temperature as in Table 1. [b] Yield of isolated product. [c] Catalyst: 1.0 mol% Pd/C. [d] Reaction time 48 h.

ployed, substitution at positions 1, 3, and 5 with both alkyl and aryl residues was achieved (entries 6–11). It should also be emphasized that 5-arylhydantoins **15**–**19** were produced in good yields, which also illustrates that a wide variety of functional groups are tolerated. In addition to the catalyst system $PdBr_2/2\,PPh_3$, palladium on activated charcoal is also able to catalyze the carbonylation efficiently (Table 2, entries 6 and 13). The latter catalyst is particularly advantageous due to the very simple separation of the catalyst after the reaction. This is especially important for potential pharmaceutical preparations of hydantoins. The only limitation of this procedure that we have discovered thus far occurred in the reaction of aldehydes of the form RCH_2CHO with urea and methylurea. Here, we isolated the 2-oxotetrahydropyrimidine as the main product.[23]

In conclusion, the palladium-catalyzed carbonylation of aldehydes with urea derivatives provides a remarkably simple, pharmacologically interesting method for the preparation of 5-, 3,5-, and 1,3,5-substituted hydantoins in good to very good yields. The excellent chemo- and regioselectivities are an important advantage of this new one-pot multicomponent reaction over classical methods. Moreover, we have also demonstrated the practicability of this method. The preparation of 47 g of 5-cyclohexyl-1,3-dimethylhydantoin (**10**) described in the Expermental Section indicates that this carbonylation procedure is also suitable for the multi-gram production of hydantoins.

Experimental Section

Synthesis of **10**: Cyclohexanecarbaldehyde (29 g, 0.25 mol), *N*,*N*′-dimethylurea (22 g, 0.25 mol), palladium dibromide (0.16 g), triphenylphosphane (0.32 g), LiBr (4.5 g), sulfuric acid (0.25 g), and *N*-methylpyrrolidone (150 mL) were transferred into a 300 mL autoclave and allowed to react under 60 bar carbon monoxide at 100 °C for 24 h. The volatile components were removed in vacuo and the residue was taken up in ethyl acetate and washed with water. The organic phase was collected and the solvent was removed in vacuo to give **10** (47 g, 0.22 mol) in >97% purity.

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Synthesis and Stereoselective Reactions of New Stable α-Ferrocenyllithium Derivatives. An Umpolung of the Ferrocene Reactivity**

Tania Ireland, Juan J. Almena Perea, and Paul Knochel*

The design of new chiral ligands for asymmetric catalysis is an important synthetic goal. In particular, ferrocenyl ligands have attracted considerable attention and numerous synthetic methods for the preparation of new ferrocenyl derivatives have been developed.[1] Many useful ferrocenyl ligands can be prepared by the nucleophilic substitution of readily available α-ferrocenylcarbinol derivatives of type **1** (Scheme 1).[1, 2] According to Ugi[2b] these substitutions proceed with retention of configuration via a chiral cationic intermediate **2** and lead to products of type **3**. Herein we report the umpolung of this reactivity. It was possible to generate α-ferrocenyllithium derivatives[3] of type **4** and to react them stereoselectively with different electrophiles to give the new chiral ferrocenyl derivatives **5** with complete retention of configuration.

In preliminary experiments the ferrocenyl thioether **6a** (95% *ee*) was treated with lithium naphthalenide (3 equiv) at

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