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Highly Selective Preparation of a Chiral Quaternary Allyl Aryl Piperidinedione by Palladium-Catalyzed Asymmetric Allylation Under Solid–Liquid Phase-Transfer Catalysis

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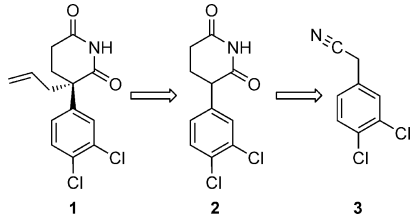
The combination of a chiral palladium catalyst and a solid–liquid phase-transfer catalyst provides an effective method for the chemo- and enantioselective preparation of the chiral quaternary center of an allyl aryl piperidinedione.

Introduction

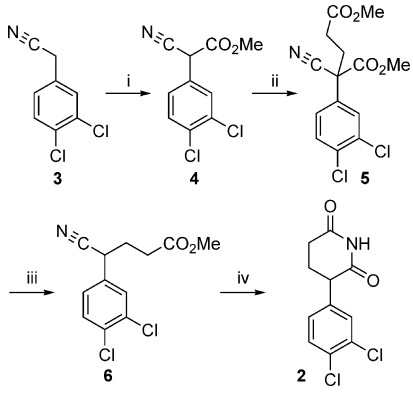
The construction of organic molecules containing chiral all-carbon quaternary stereocenters by enantioselective catalysis represents a very challenging area in organic synthesis.[1] Among the many suitable reactions, asymmetric allylic alkylation (AAA) is a very attractive and powerful synthetic strategy, as it enables the direct and stereocontrolled formation of chiral quaternary centers bearing a diversity of functionalities available for further structural elaboration.[2] In intermolecular palladium-catalyzed AAA, success in preparing chiral quaternary stereocenters has been obtained with prochiral enolates as the nucleophiles, which were generated from, for instance, β-diketones,[3] β-keto esters,[4] α-acetamido-β-keto esters and related derivatives,[5] iminoesters,[6] cyclic ketones,[7] and lactams.[8]

We have an interest in the preparation of intermediates containing a chiral quaternary center.[9] We prepared allyl aryl cyano esters with moderate selectivity by AAA.[9] We pursued our investigations with the purpose to prepare chiral aryl allyl glutarimide[10] by direct alkylation of glutarimide enolate. Chiral glutarimide contains a quaternary stereocenter, and it is of interest for further elaboration of this compound into piperidine intermediates, which are building blocks of high synthetic utility that are present in biologically active compounds.[11] Imides have been applied in the AAA reaction. Nevertheless, essentially intramolecular *N*-alkylation has been used in total synthesis.[2c]

Here, we report on the preparation of chiral intermediate **1** by AAA of **2** (Scheme 1). The latter was prepared in a few steps starting from (3,4-dichlorophenyl)acetonitrile (**3**; Scheme 2).



Scheme 1. Retrosynthesis of **1**.



Scheme 2. Synthesis of **2**. Reagents and conditions: (i) NaOMe, dimethylcarbonate, toluene, reflux, 93%; (ii) methyl acrylate, Triton B, THF, reflux, 85%; (iii) LiOH, THF, reflux, 85%; (iv) AcOH, H_2SO_4 (10 mol-%), reflux, 86%.

Results and Discussion

Our synthesis (Scheme 2) began with the substitution at the benzylic position of **3** through reaction with dimethyl-

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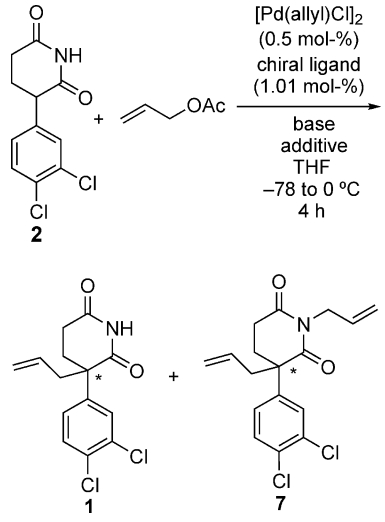
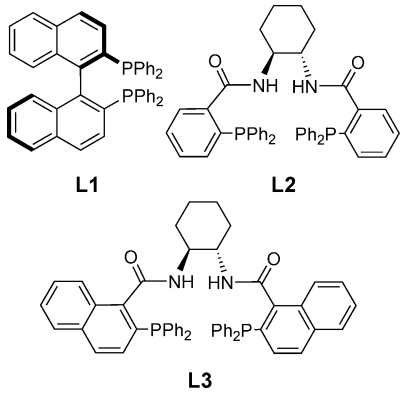
carbonate in the presence of sodium methoxide in toluene (2 equiv.).[12] Michael addition was carried out next in the presence of methyl acrylate and benzyltrimethylammonium hydroxide (Triton B) to afford **5** in 85% isolated yield. Then, **5** was transformed into γ-cyano ester **6** through demethoxycarbonylation performed in THF under reflux in the presence of lithine. Compound **6** was isolated in 85% yield.

Finally, γ-cyano ester **6** was converted into imide **2** through heating in glacial acetic acid in the presence of a catalytic amount of H_2SO_4,[13] and **2** was isolated, after purification, in 86% yield. Compound **2** was next used in palladium-catalyzed AAA (Scheme 3). The results are reported in Table 1. With substrate **2**, we encountered a selectivity problem during the AAA as *C*- as well as *N*-alkylation can occur. Indeed, preliminary experiments carried out in the presence of allyl acetate, NaH (1.5 equiv.), and a catalytic amount of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.5 mol-%) and (*R*)-BINAP (**L1**, 1 mol-%) provided a mixture of mono- and bis(allyl) products **1** and **7** (60% conversion, **1**/**7**, 1:1), respectively, as determined by ^{1}H NMR spectroscopy (Table 1, Entry 1). After workup, expected product **1** was isolated in a low yield of 9% and with 15% *ee* (determined by ^{13}C NMR spectroscopy in the presence of a chiral shift reagent).



Scheme 3. Palladium-catalyzed alkylation.

The use of identical reaction conditions in the presence of Trost auxiliaries **L2** and **L3** (Scheme 4) resulted in a mixture of **1** and **7** (Table 1, Entries 2 and 3). Interestingly, the enantioselectivity introduced into **1** increased from 15 to 40 and then to 80% *ee* when ligands **L1**, **L2**, and **L3** were used, respectively. Several bases were used (LDA, Cs_2CO_3, and KH) (Table 1, Entries 4–6) without providing higher selectivities of **1** in the presence of **L3**.



Scheme 4. Chiral auxiliaries.

In order to increase the selectivity of **1**, we attempted to bring into solution a more reactive *C*-nucleophile that was also deprotonated at the imide position, which would thus favor *C*-allylation over *N*-allylation. We performed the AAA in the presence of a catalytic amount of nHex$_4$NBr (10 mol-%). The conversion and the isolated yield of **1** were higher (Table 1, Entry 7), even if the selectivity was still not satisfactory (88% conversion, 45% isolated yield of **1**). When the amount of base was increased to two equivalents, imide **2** was converted totally into the insoluble bis(anion). Again, the latter was brought into solution under solid–liquid phase-transfer catalysis in the presence of a catalytic amount of nHex$_4$NBr (10 mol-%) allowing the most reactive *C*-nucleophile to react selectively.[14] We were delighted to observe high conversion of the substrate accompanied by total selectivity into the mono *C*-alkyl product **1**. Product

Table 1. Enantioselective allylation of **2** catalyzed by chiral palladium complexes.[a]

Entry	Chiral ligand	Base[b] [equiv.]	Additive[b] [equiv.]	Conversion[c] [%]	Yield **1**[d] [%]	*ee* of **1** [%] (configuration)[e]
1	**L1**	NaH (1.5)	–	60	9	15 (*R*)
2	**L2**	NaH (1.5)	–	50	10	40 (*R*)
3	**L3**	NaH (1.5)	–	59	30	80 (*R*)
4	**L3**	LDA (1.5)	–	55	25	50 (*R*)
5	**L3**	Cs_2CO_3 (1.5)	–	60	29	80 (*R*)
6	**L3**	KH (1.5)	–	60	30	79 (*R*)
7	**L2**	NaH (1.5)	nHex$_4$NBr (0.1)	75	35	40 (*R*)
8	**L3**	NaH (1.5)	nHex$_4$NBr (0.1)	88	45	80 (*R*)
9	**L3**	NaH (2)	nHex$_4$NBr (0.1)	95	95	80 (*R*)

[a] AAA reactions were carried out in THF with Pd/chiral auxiliary/**2**, 1:1:100. [b] Amount of base and additive with respect to **2**. [c] Determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixtures. [d] Determined after isolation of **1** through silica gel chromatography. [e] Determined by ^{13}C NMR spectroscopy in the presence of Eu(hfc)$_3$. Configuration attributed according to the negative sign of rotation measured by polarimetry.[10]

1 was isolated in 95% yield and with 80% optical purity. Thus, *C*-alkylation is kinetically favored under our experimental conditions. The added ammonium salt acts as a phase-transfer catalyst, which brings the insoluble enolate into solution to favor the kinetic process of *C*-alkylation. Under such conditions, no *N*-alkylation is detectable.

Conclusions

We developed an efficient method for the selective alkylation of an aryl glutarimide enolate providing an allyl derivative bearing a sterically congested quaternary stereocenter with the aid of two catalytic processes (organometallic and phase-transfer). This methodology is of interest to solve some selectivity issues in AAA reactions. This combined catalysis is under investigation for the preparation of other chiral intermediates of interest bearing a quaternary carbon and results will be reported soon.

Experimental Section

All melting points were measured with an Electrothermal IA9300 melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded with a BRUKER AC300 spectrometer at 25 °C. Chemical shifts are reported in ppm downfield of internal tetramethylsilane. GPC analyses were conducted with a CHROMPACK CP 9000 apparatus equipped with a BPX5 capillary column (25 × 0.32 mm). All reagents are commercially available and were used without further purification. The organic syntheses were carried out under classical conditions unless otherwise stated. The reactions were performed under an atmosphere of nitrogen. THF was dried with $CaCl_2$, filtered through basic alumina and distilled from Na/K under an atmosphere of nitrogen. Diethyl ether was distilled from sodium under an atmosphere of nitrogen.

Methyl Cyano(3,4-dichlorophenyl)acetate (4): To a 200-mL round-bottom flask equipped with a condenser and a stir bar was added sodium methoxide (3.45 g, 64 mmol), (3,4-dichlorophenyl)acetonitrile (**3**; 10.2 g, 55 mmol), and dimethylcarbonate (18 mL, 212 mmol) followed by toluene (25 mL). The reaction mixture was heated to 85 °C for 3 h during which time a slurry formed. Toluene was distilled from the reaction medium under reduced pressure. Then, the reaction mixture was hydrolyzed with HCl (1 N). Cyanoester **4** was extracted with diethyl ether (100 mL and then 2 × 70 mL). The combined organic layer was washed with water (2 × 100 mL), brine (100 mL), and dried with anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, the product was isolated as a brown solid (12.48 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, CH_3), 4.69 (s, 1 H, CHCN), 7.31 (dd, $^3J_{H,H}$ = 2.3 and 8.3 Hz, 1 H, H_{Ar}), 7.50 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, H_{Ar}), 7.56 (d, $^3J_{H,H}$ = 2.3 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 42.5 (*C*HCN), 54.3 (O*C*H$_3$), 114.7 (*C*N), 127.3, 129.6, 130.0, 131.3, 133.6, and 134.0 (C_{Ar}), 164.6 (CO) ppm. $C_{10}H_7Cl_2NO_2$ (244.08): calcd. C 49.20, H 2.89, N 5.74; found C 49.18, H 2.81, N 5.67.

Dimethyl 2-Cyano-2-(3,4-dichlorophenyl)pentanedioate (5): To a 250-mL round-bottom flask equipped with a condenser and a stir bar was added **4** (13.42 g, 55 mmol) and THF (125 mL) with Triton B (1.94 mL, 11 mmol) followed by methyl acrylate (13.5 mL, 148.5 mmol). The reaction mixture was heated at reflux for 23 h. After cooling and evaporation of THF under reduced pressure, the oily residue was dissolved in ethyl acetate (100 mL) and washed with water (75 mL). The aqueous phase was washed with ethyl acetate (3 × 50 mL). The combined organic phase was washed with brine (3 × 75 mL) and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The product was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 9:1 then 4:1). Derivative **5** was isolated as a yellow solid (14.41 g, 84%). R_f = 0.44 (ethyl acetate/petroleum ether, 1:4). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35–2.71 (m, 4 H, 2 C*H*$_2$), 3.65 (s, 3 H, OC*H*$_3$), 3.80 (s, 3 H, OC*H*$_3$), 7.38 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 2.2 Hz, 1 H, H_{Ar}), 7.49 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, H_{Ar}), 7.62 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.0 (*C*H$_2$), 33.0 (*C*H$_2$), 52.0 (O*C*H$_3$), 52.3 (*C*CN), 54.4 (O*C*H$_3$), 116.9 (*C*N), 125.5, 128.3, 131.2, 133.6, 133.7, 13.9 (C_{Ar}), 166.8 (*C*O), 171.6 (*C*O) ppm. $C_{14}H_{13}Cl_2NO_4$ (330.17): calcd. C 51.40, H 4.00, N 3.36; found C 51.25, H 3.89, N 3.40.

Methyl 4-Cyano-4-(3,4-dichlorophenyl)butyrate (6): To a 250-mL round-bottom flask equipped with a condenser and a stir bar was added **5** (7.664 g, 23.2 mmol) dissolved in THF (110 mL) followed by lithium hydroxide (1.05 g, 25 mmol). The reaction mixture was heated at reflux for 18 h, and the evolution of the reaction was followed by GC. If necessary, more lithium hydroxide was added (0.25-equiv. portions) until total conversion. After cooling, THF was removed under reduced pressure. The oily residue was dissolved in ethyl acetate (100 mL) and washed with HCl (1 N, 3 × 50 mL). The aqueous phase was washed with ethyl acetate (3 × 50 mL). The combined organic phase was washed with brine (3 × 100 mL) and dried with anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, the product was purified by flash silica gel chromatography (petroleum ether/ethyl acetate, 9:1 then 4:1). Derivative **6** was isolated as a yellow crystalline solid (5.43 g, 86%). M.p. 106 °C. R_f = 0.45 (ethyl acetate/petroleum ether, 1:4). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.13–2.20 (m, 2 H, C*H*$_2$COOMe), 2.40–2.59 (m, 2 H, CNCHC*H*$_2$), 3.67 (s, 3 H, OCH$_3$), 4.0 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, CHCN), 7.18 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, H_{Ar}), 7.43–7.47 (m, 2 H, H_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.6 (2*C*H$_2$), 35.5 (*C*HCN), 52.0 (O*C*H$_3$), 119.3 (*C*N), 126.6, 129.3, 131.2, 132.8, 133.4, 135.2 (C_{Ar}), 17.22 (*C*O) ppm. $C_{12}H_{11}Cl_2NO_2$ (272.13): calcd. C 52.96, H 4.07, N 5.15; found C 52.51, H 3.95, N 5.12.

3-(3,4-Dichlorophenyl)piperidinedione (2): To a 100-mL round-bottom flask equipped with a condenser and a stir bar was added **6** (3 g, 11.1 mmol) dissolved in acetic acid (15 mL). Then, concentrated sulfuric acid (600 μL) was added dropwise. The reaction mixture was heated at reflux for 18 h. After cooling, the reaction mixture was hydrolyzed with a saturated solution of $NaHCO_3$. The medium was extracted with dichloromethane (2 × 75 mL). The combined organic phase was washed with brine (3 × 75 mL) and dried with anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, the product was crystallized from dichloromethane and isolated as white crystals (2.26 g, 92%). M.p. 207 °C. ^{1}H NMR (300 MHz, DMSO): δ = 1.96–2.01 (m, 1 H, CH_{dione}), 2.01–2.27 (m, 1 H, CH_{dione}), 2.49–2.54 (m, 1 H, CH_{dione}), 2.62–2.68 (m, 1 H, CH_{dione}), 3.96 (dd, $^3J_{H,H}$ = 12.4 Hz, $^4J_{H,H}$ = 4.6 Hz, 1 H, C*H*CONH), 7.23–7.28 (m, 1 H, H_{Ar}), 7.56–7.62 (m, 2 H, H_{Ar}), 10.91 (s, 1 H, N*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.4 (CH_2), 31.6 (CH_2), 46.5 (CH), 129.3, 129.6, 130.2, 130.4, 130.8, 140.2 (C_{Ar}), 171.5 (CO), 172.1 (CO) ppm. $C_{11}H_9Cl_2NO_2$ (258.10): calcd. C 51.19, H 3.51, N 5.43; found C 50.88, H 3.47, N 5.43.

3-(*S*)-Allyl-3-(3,4-dichlorophenyl)piperidine-2,6-dione (1): In a Schlenk tube, glutarimide **2** (258.1 mg, 1 mmol) was dissolved in THF (4 mL). The solution was cooled to –78 °C and NaH (48 mg,

2 mmol) was added. The solution was stirred at –78 °C for 1 h and then charged with a solution containing $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.8 mg, 0.005 mmol), chiral auxiliary **L3** (7.9 g, 0.01 mmol), allyl acetate (220.6 mg, 2.2 mmol), and tetrabutylammonium bromide (32.2 mg, 0.1 mmol) in THF (2 mL). The cold bath was removed, and the reaction mixture was stirred at 0 °C for 4 h. The reaction mixture was quenched with saturated NH_4Cl (5 mL) and then water (10 mL). The organic phase was extracted with ethyl acetate (3 × 15 mL), washed with brine (3 × 20 mL), dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 2:1). Product **1** was isolated as a white crystals (283.3 mg, 95%). M.p. 137 °C. R_f = 0.6 (ethyl acetate/petroleum ether, 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.22–2.41 (m, 3 H, CH_{dione}), 2.48–2.65 (m, 2 H, CHH′CH= and CH_{dione}), 2.75–2.81 (m, 1 H, CHH'CH=CH$_2$), 5.05–5.13 (m, 2 H, CH=CH_2), 5.59 (m, 1 H, CH=CH$_2$), 7.13 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.2 Hz, 1 H, H$_{Ar}$), 7.38 (d, $^4J_{H,H}$ = 2.2 Hz, 1 H, H$_{Ar}$), 7.43 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, H$_{Ar}$), 8.5 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.1 (CH$_2$), 29.0 (CH$_2$), 44.3 (CH$_2$), 50.0 (C), 120.2 (CH=CH$_2$), 125.7 (CH=CH$_2$), 128.4, 131.0, 132.2, 133.4, 138.7 (C$_{Ar}$), 172.0 (CO), 173.9 (CO) ppm. $C_{14}H_{13}Cl_2NO_2$ (298.17): calcd. C 56.39, H 4.39, N 4.70; found C 56.16, H 4.44, N 4.54.

1,3-Diallyl-3-(*S*)-(3,4-dichlorophenyl)piperidine-2,6-dione (7): In a Schlenk tube, glutarimide **2** (258.1 mg, 1 mmol) was dissolved in THF (4 mL). The solution was cooled to –78 °C and NaH (48 mg, 2 mmol) was added. The solution was stirred at –78 °C for 1 h and then charged with a solution containing $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.8 mg, 0.005 mmol), chiral auxiliary **L3** (7.9 g, 0.01 mmol), and allyl acetate (300 mg, 2.5 mmol) in THF (2 mL). The cold bath was removed, and the reaction mixture was stirred at 0 °C for 4 h. The reaction mixture was quenched with saturated NH_4Cl (5 mL) and then water (10 mL). The organic phase was extracted with ethyl acetate (3 × 15 mL), washed with brine (3 × 20 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate, 2:1). Product **7** was isolated as a yellow oil (270 mg, 80%). R_f = 0.82 (ethyl acetate/petroleum ether, 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20–2.23 (m, 2 H, CH_{2dione}), 2.36–2.54 (m, 2 H, CH_{2dione}), 2.71 (m, 1 H, CCHH′CH=CH$_2$), 2.77 (m, 1 H, CCHH'CH=CH$_2$), 4.4 (m, 2 H, NCH_2CH=CH$_2$), 5.01–5.16 (m, 4 H, CH$_2$CH=CH_2), 5.52–5.69 (m, 1 H, CH$_2$CH=CH$_2$), 5.7–5.81 (m, 1 H, CH$_2$CH=CH$_2$), 7.03 (dd, $^3J_{H,H}$ = 8.52 Hz, $^4J_{H,H}$ = 1.95 Hz, 1 H, H_{Ar}), 7.29 (d, $^4J_{H,H}$ = 1.95 Hz, 1 H, H_{Ar}), 7.39 (d, $^3J_{H,H}$ = 8.52 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1 (CH$_{2dione}$), 29.5 (CH$_{2dione}$), 42.2 (CCH$_2$CH=CH$_2$), 45.2 (NCH$_2$CH=CH$_2$), 50.4 [C(CO)(CH$_2$)(CH$_2$)], 118 (CH$_2$=CH), 120 (CH$_2$=CH), 125.7 (CH$_2$=CH), 128.5 (CH$_2$=CH), 130,9; 131,8; 131.9, 132.5, 133.3, 139.3 (C_{Ar}), 171 (C=O), 173.4 (C=O) ppm. $C_{17}H_{17}Cl_2NO_2$ (338.23): calcd. C 60.37, H 5.07, N 4.14; found C 60.01, H 4.97, N 4.34.

Acknowledgments

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