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Palladium-catalyzed allylic alkylation using pyridino-oxazolines and quinolino-oxazolines as ligands — influence of steric factors

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Abstract

Four new chiral pyridino- and quinolino-oxazolines were subjected to the palladium-catalyzed alkylation of 1,3-diphenyl-2-propenyl acetate. The enantioselectivity varied (82–88% ee) with the steric properties of the ligands. The results are discussed in connection with results previously obtained using analogous ligands. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Asymmetric metal catalysis constitutes one of the most versatile methods for the preparation of chiral compounds in enantiomerically pure form.[1] In order to enable rational design of the metal complexes responsible for the catalytic activity, a profound understanding of the factors governing the catalytic process is required.

The palladium-catalyzed allylic alkylation reaction is a particularly useful catalytic process in that a carbon–carbon bond is formed in the reaction.[2] A variety of *P*,*P*-, *P*,*N*- and *N*,*N*-based ligands, with C_1[3] as well as C_2 symmetry,[4] have proven to induce high selectivity in the process.

Pyridino-oxazolines have been used with varying success as ligands in the reaction of *rac*-1,3-diphenyl-2-propenyl acetate **1** with dimethyl malonate to yield **2** (Scheme 1). With (4′*R*)-2-(4′,5′-dihydro-4′-phenyl-2′-oxazolyl)pyridine **3a**, only moderate stereoselectivity (50–55% ee of the product with *R* configuration) was observed.[5,6] We and others have shown that modification of the structure of the ligand may have a profound effect on the outcome of the reaction. Thus, the introduction of a methyl group in the 6-position of the pyridine ring **3b** had the effect of increasing the ee to 74%.[6] Dramatic effects were observed with hydroxyalkyl and methoxyalkyl substituents (compounds **3c**–**3f**, Scheme 1).[5] Formation of the product with *R* configuration was always favored, but the selectivity varied (15–>99% ee) with the structure and absolute configuration of the substituent.

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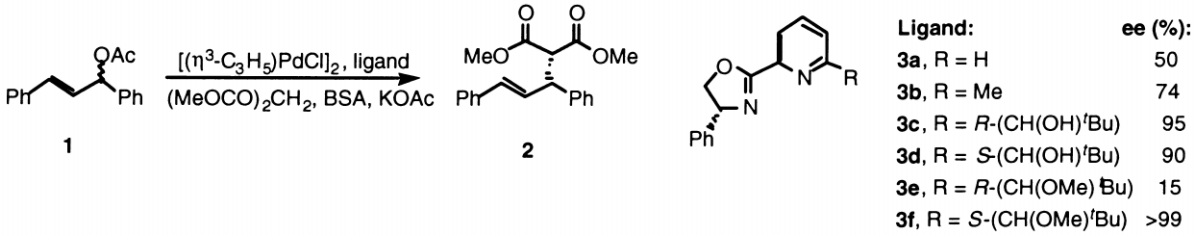


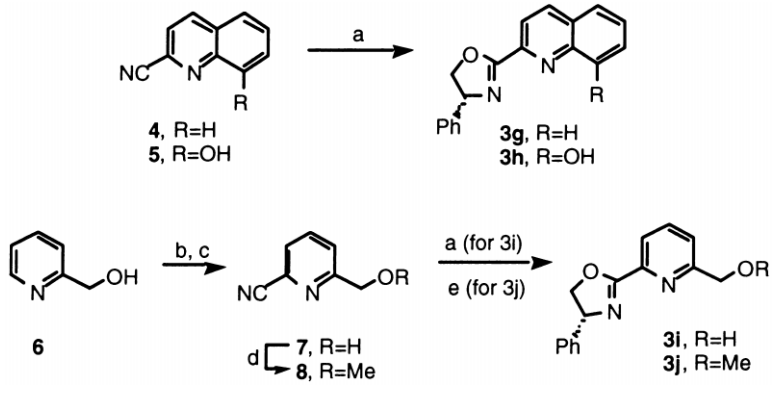
Scheme 1.

In order to gain a deeper insight into the factors responsible for the stereoselectivity of the reaction, some new pyridino-oxazolines and quinolino-oxazolines have been prepared and subjected to the catalytic reaction.

2. Results and discussion

2.1. Preparation of ligands

2-Oxazolinylquinolines **3g** and **3h** were prepared from (*R*)-2-phenylglycinol and 2-cyanoquinolines **4** and **5**,[7,8] respectively, using copper chloride as catalyst† (Scheme 2). The pyridine derivative **3i** was synthesized starting from 2-(hydroxymethyl)pyridine **6** via nitrile **7**, which was subsequently transformed to the target oxazoline via the process described above. Attempts to *O*-methylate **3i** using either sodium hydride and methyl iodide in THF or potassium hydroxide and methyl iodide in DMSO[9] resulted in low yields of the desired product **3j**. Therefore, a route for the preparation of **3j** involving methylation of **7** (to give **8**) and subsequent introduction of the oxazoline ring was preferred. In this case, a sequence involving initial reaction of the nitrile with methoxide and subsequent transformation of the obtained imidate to an oxazoline was found to be more convenient and to result in a higher yield than the copper chloride-catalyzed process.



Scheme 2. (a) (*R*)-Phenylglycinol, $CuCl_2$, neat 100°C, 10 mbar; (b) *m*-CPBA, $CHCl_3$, rt, 24 h; (c) TMSCN, *N*,*N*-dimethylcarbamoyl chloride, CH_2Cl_2, reflux, 37 h; (d) NaH, MeI, THF, rt, 16 h; (e) (1) NaOMe, MeOH, rt, 28 h; (2) (*R*)-phenylglycinol, H_2SO_4 (cat.), CH_2Cl_2, reflux, 24 h

† Problems were encountered during attempts to transform the nitrile **5** to an oxazoline with standard methods. The rarely used catalyst $CuCl_2$ (Breslow, R.; Schmir, M. *J. Am. Chem. Soc*. **1971**, *93*, 4960–4961) worked satisfactorily though.

2.2. Palladium-catalyzed allylic alkylation

Allylic substitution of *rac*-1,3-diphenyl-2-propenyl acetate **1** was performed in dichloromethane at room temperature in the presence of a π-allylpalladium–ligand complex generated in situ from 2 mol% of bis[η^3-allylpalladium chloride] and 6 mol% of the appropriate ligand. The nucleophile was generated from dimethyl malonate in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of KOAc.[4b] The chemical yields were high when **3g**, **3i** and **3j** were employed as ligands, (99, 93 and 99% of **2**, respectively), while no product was obtained upon use of the hydroxy derivative **3h**. The product with *R* configuration dominated in the reactions. The selectivity observed when quinoline compound **3g** was employed as ligand was higher (73% ee) than that observed with the corresponding pyridine ligand **3a** (50% ee). Catalytic reactions with the pyridine ligands **3i** and **3j** were also more selective than those employing **3a**, affording the product with 88 and 82% ee, respectively.

2.3. Stereochemistry of the reaction and conformation of the ligands

With C_1-symmetric ligands, such as **3a**–**3j**, two *syn*,*syn*-π-allylpalladium complexes may form and the two complexes are usually also observed (together with small amounts of the *syn*,*anti* isomers). The site of nucleophilic attack on each complex determines the absolute configuration of the product. Since equilibration between the isomeric complexes is rapid compared to the attack of the nucleophile on the complex, the ratio of the complexes does not directly reflect the ratio of the products.[10] What is usually observed, however, is that product formation from the most abundant complex is preferred.

The regiochemistry of attack at each complex is influenced by electronic as well as steric factors.[11] The bond lengths between the carbon atoms of the allylic termini and palladium are influenced by the ligand *trans* to the carbon atom (*trans* influence) as well as by steric effects exerted by the ligand, and a longer bond to palladium will result in higher reactivity.[12] With bidentate ligands containing donor atoms with similar properties, steric factors are assumed to be most important.

Due to hydrogen bonding, pyridine ligands with a hydroxymethyl group in 2-position of the pyridine ring (such as **3c** and **3d**) adopt a conformation in which the carbon–oxygen bond of the substituent is situated in the plane of the pyridine ring, with the oxygen atom *syn* to nitrogen. In their most stable conformation, ligands containing a methoxymethyl group (such as **3e** and **3f**) also have the carbon–oxygen bond of the substituent close to the plane of the pyridine ring, but with the oxygen atom *anti* to nitrogen.[13] We have shown that the ligands also adopt similar conformations in their complexes with palladium, thereby permitting the enantioselectivity of ligands **3c**–**3f** to be rationalized. It should be noted that since no product was formed in the presence of ligand **3h** where the hydroxy group is forced to be in the plane of the heterocyclic ring, ligands **3c**, **3d** and **3i** probably adopt conformations where the carbon–oxygen bond is close to but not exactly in that plane.

The enantioselectivity observed for pyridino-oxazolines containing 1-hydroxyalkyl substituents in the 6-position of the pyridine ring varied only slightly with the structure of the substituent (88% ee for R=R′=H, 95% ee for R=H, R′=^{t}Bu, and 90% ee for R=^{t}Bu, R′=H, A, Fig. 1). The reason for this is probably that in the preferred conformation of the ligand, the R and R′ groups are remote from the allyl group and therefore only have a minor influence on its position. However, dramatic effects were observed for ligands with a 1-methoxyalkyl substituent on the pyridine ring (82% ee for R=R′=H, 15% ee for R=H, R′=^{t}Bu, and >99% ee for R=^{t}Bu, R′=H, B, Fig. 1). In these ligands the R and R′ groups are close to the allyl group and thus exert an important influence on its position. It is also interesting to note that a ligand with a hydroxymethyl substituent in the 6-position of the pyridine ring **3i** results in higher selectivity

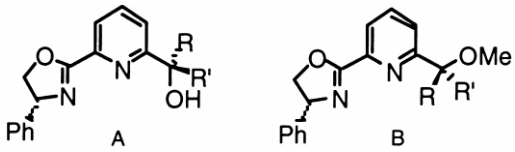


Fig. 1. Conformation of ligands **3i**, **3c** and **3d** (A) and of **3j**, **3e** and **3f** (B)

(88% ee) than ligands with a methoxymethyl (82%) or a methyl group (74% ee) in that position, the latter with a selectivity similar to that of the quinolino-oxazoline (73% ee).

3. Conclusions

The enantioselectivity of the palladium-catalyzed alkylation of *rac*-1,3-diphenyl-2-propenyl acetate with dimethyl malonate using chiral pyridino-oxazolines and quinolino-oxazolines as ligands is highly dependent on the structure of the ligands. The substituent in the 6-position of the pyridine ring of the pyridino-oxazolines has a particularly large influence on the selectivity. The results can be rationalized considering the conformation of the ligand in the reactive palladium complexes.

4. Experimental

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100.6 MHz, respectively, in $CDCl_3$. THF was distilled from sodium/benzophenone.

4.1. 2-Cyano-6-(hydroxymethyl)pyridine **7**

m-CPBA (34.50 g, 55%, 110 mmol) was added to 2-(hydroxymethyl)pyridine (10.00 g, 91.6 mmol) in chloroform (150 mL) at 0°C during 30 min. The suspension was stirred at rt for 24 h. Residual *m*-CPBA was destroyed by the addition of paraformaldehyde (2.0 g, 66.6 mmol CH_2O equivalents). After stirring for 2 h, ammonia was bubbled through the reaction mixture for 10 min. The thick suspension was dried (Na_2SO_4) and filtered and the filter cake washed with dichloromethane (250 mL). The solid residue was continuously extracted with the filtrate for 63 h. Evaporation of the solvent yielded 11.24 g (98%) of 2-(hydroxymethyl)pyridine-*N*-oxide. ^{1}H NMR δ 8.25 (1H, d, *J*=6.1 Hz, H6), 7.36–7.26 (3H, m, H3, H4, H5), 4.80 (2H, s, CH_2). The signal for the hydroxy proton was not observed.

The *N*-oxide (1.255 g, 10.03 mmol) was partially dissolved in dichloromethane (25 mL) and *N*,*N*-dimethylcarbamoyl chloride (923 μL, 10.03 mmol) was added over 5 min. After stirring for 90 min, more dichloromethane (15 mL) was added and the mixture was heated to reflux for 90 min. The reaction mixture was allowed to cool to rt, whereafter trimethylsilyl cyanide (1.61 mL, 12.04 mmol) was added dropwise, and the mixture was heated to reflux for a further 14 h. The mixture was allowed to cool to rt before additional *N*,*N*-dimethylcarbamoyl chloride (923 μL, 10.03 mmol) and trimethylsilyl cyanide (1.34 mL, 10.03 mmol) were added. After 22 h at reflux, the reaction was quenched by the addition of saturated aqueous Na_2CO_3 (25 mL). The phases were separated, the aqueous phase was extracted with dichloromethane (3×25 mL) and the combined organic phases were dried ($MgSO_4$). Evaporation of the solvent gave a brown liquid which was purified by chromatography on silica gel (8×4 cm column, ethyl acetate:hexanes=1:1, followed by ethyl acetate) to give the expected product **7** (307 mg, 23%) and the corresponding silylated alcohol (826 mg, 40%). The silylated alcohol was deprotected using aqueous HF in acetonitrile[14] and purified by chromatography with a smooth exponential gradient of ethyl acetate in

hexanes to yield **7** (365 mg, 68%). Total yield: 672 mg, 50%. ^{1}H NMR δ 7.85 (1H, t, *J*=7.8 Hz, H4), 7.63 (1H, d, *J*=7.6 Hz, H3), 7.55 (1H, d, *J*=7.6 Hz, H5), 4.83 (2H, d, *J*=5.2 Hz, CH_2), 3.12 (1H, t, *J*=5.5 Hz, OH).

*4.2. 2-Cyano-6-(methoxymethyl)pyridine **8***

Nitrile **7** (100 mg, 0.15 mmol) in THF (5 mL) was added to NaH (35.8 mg, 60% in mineral oil, 0.89 mmol, washed with dry hexane) in THF (5 mL) at 0°C under nitrogen. The mixture was stirred for several min, whereafter MeI (74.3 μL, 1.2 mmol) was added dropwise. A drying tube was fitted, and the mixture was stirred overnight on the thawing ice bath. The mixture was diluted with diethyl ether (25 mL) and the organic phase washed with water followed by saturated aqueous NH_4Cl. The aqueous phases were extracted with diethyl ether (2×25 mL), and the combined organic phases were dried (Na_2SO_4). Evaporation of the solvent gave a yellow solid which, after chromatography on silica gel (8×3 cm column, ethyl acetate:hexanes=3:7), yielded 53 mg (48%) of **8**. ^{1}H NMR δ 7.85 (1H, t, *J*=7.8 Hz, H4), 7.68 (1H, d, *J*=7.7 Hz, H3), 7.60 (1H, d, *J*=7.3 Hz, H5), 4.61 (2H, s, CH_2), 3.49 (3H, s, OCH_3).

4.3. General procedure for oxazoline synthesis

The nitrile (1 equiv.) was mixed with (*R*)-phenylglycinol (**3g**, **3h**: 1.5 equiv.; **3i**: 2.0 equiv.) and $CuCl_2$ (0.05 equiv.) under dry conditions. The neat reaction mixture was stirred at 100°C at reduced pressure (10 mbar)[‡] for a time depending on the individual nitriles. Sublimed amino alcohol occasionally had to be scraped down into the reaction mixture from vessel walls. Continuous extraction with hexanes for at least 48 h, followed by chromatography on silica gel with ethyl acetate (for **3i**) or a smooth exponential gradient of ethyl acetate in hexanes (for **3g** and **3h**), yielded the desired oxazoline.

*4.3.1. (4′R)-2-(4′,5′-Dihydro-4′-phenyl-2′-oxazolyl)quinoline **3g***

Yield: 82%; powder, mp 140.5–142.5°C (from hexanes:ethyl acetate:benzene); $[\alpha]_D^{20}$ +160 (c 0.74, $CHCl_3$); ^{1}H NMR δ 8.29 (2H, bd, *J*=8.5 Hz, H4, H8), 8.24 (1H, dd, *J*=8.6, 0.9 Hz, H3), 7.86 (1H, ddd, *J*=8.2, 1.6, 0.7 Hz, H5), 7.77 (1H, ddd, *J*=8.5, 6.8, 1.6 Hz, H7), 7.61 (1H, ddd, *J*=8.1, 6.9, 1.2 Hz, H6), 7.26–7.40 (5H, m, arom. H), 5.52 (1H, dd, *J*=10.2, 8.7 Hz, H5′), 4.99 (1H, dd, *J*=10.4, 8.5 Hz, H5′), 4.48 (1H, t, *J*=8.6 Hz, H4′); ^{13}C NMR δ 164.2, 147.7, 146.8, 141.8, 136.9, 130.5, 130.2, 128.9 (2C), 128.1, 127.9, 127.6, 126.9, 121.1, 75.7, 70.5; Anal. calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.56; H, 5.16; N, 10.14.

*4.3.2. (4′R)-2-(4′,5′-Dihydro-4′-phenyl-2′-oxazolyl)-8-hydroxyquinoline **3h***

Yield: 55%; powder, mp 132.5–135°C (from hexanes); $[\alpha]_D^{20}$ −102 (c 0.53, $CHCl_3$); ^{1}H NMR δ 8.35 (1H, s, OH), 8.26 (1H, d, *J*=8.5 Hz, H3 or H4), 8.25 (1H, d, *J*=8.5 Hz, H3 or H4), 7.54 (1H, dd, *J*=8.2, 7.6 Hz, H6), 7.28–7.42 (6H, m, arom. H, H5), 7.24 (1H, dd, *J*=7.6, 1.2 Hz, H7), 5.52 (1H, dd, *J*=10.1, 8.5 Hz, H5′), 4.95 (1H, dd, *J*=10.4, 8.5 Hz, H5′), 4.44 (1H, t, *J*=8.5, H4′); ^{13}C NMR δ 164.0, 153.0, 144.3, 141.7, 137.8, 136.9, 129.6, 129.3, 128.9, 127.9, 126.9, 121.7, 117.8, 111.0, 75.5, 70.5; Anal. calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.30; H, 4.76; N, 9.60.

[‡] Serves to remove the NH_3 evolved.

*4.3.3. (4′R)-2-(4′,5′-Dihydro-4′-phenyl-2′-oxazolyl)-6-(hydroxymethyl)pyridine **3i***

Yield: 44%, 95% pure (contaminated by **6**) according to NMR. An analytically pure sample was obtained by recrystallization from diethyl ether at −78°C: oil at rt, $[\alpha]_D^{20}$ +34 (c 0.86, $CHCl_3$); ^{1}H NMR δ 8.00 (1H, d, *J*=7.6 Hz, H3), 7.76 (1H, t, *J*=7.6 Hz, H4), 7.48 (1H, d, *J*=7.6 Hz, H5), 7.27–7.35 (5H, m, arom. H), 5.41 (1H, dd, *J*=10.2, 8.7 Hz, H5′), 4.86 (1H, dd, *J*=10.2, 8.7 Hz, H5′), 4.83 (2H, s, CH_2), 4.36 (1H, t, *J*=8.6 Hz, H4′). The signal for the hydroxy proton was not observed. ^{13}C NMR δ 163.9, 160.3, 145.7, 141.8, 137.4, 128.9, 127.8, 126.8, 123.0, 122.9, 75.5, 70.3, 64.8; Anal. calcd for $C_{15}H_{14}O_2N_2$: C, 70.9; H, 5.5; N, 11.0. Found C, 70.61; H, 5.40; N, 10.86.

*4.3.4. (4′R)-2-(4′,5′-Dihydro-4′-phenyl-2′-oxazolyl)-6-(methoxymethyl)pyridine **3j***

NaOMe (2.8 mg, 0.05 mmol) was added to a solution of **8** (76 mg, 0.52 mmol) in MeOH (2 mL). The mixture was stirred under nitrogen at rt for 19 h, whereafter more NaOMe (2.8 mg, 0.05 mmol) was added and the mixture was stirred for a further 10 h. The reaction was quenched by addition of acetic acid (6 μL, 0.1 mmol) and the solvent was evaporated. The intermediate imidate was dried *in vacuo* overnight and used without further purification. To a solution of the imidate in dichloromethane (2 mL), (*R*)-phenylglycinol (71 mg, 0.52 mmol) in dichloromethane (2 mL) and one drop of concentrated H_2SO_4 were added and the mixture was stirred at reflux for 3 days. The suspension was then diluted with dichloromethane (6 mL) and washed with saturated aqueous Na_2CO_3 (8 mL). The aqueous phase was extracted with dichloromethane (3×8 mL) and the combined organic layers were dried (Na_2SO_4). Evaporation of the solvent gave a yellow liquid which was purified by chromatography on silica gel (6×2.5 cm column, ethyl acetate:hexanes=4:1, followed by ethyl acetate) to give the expected product **3j** (55 mg, 40%) as a colorless oil. $[\alpha]_D^{20}$ +70 (c 1.14, $CHCl_3$); ^{1}H NMR δ 8.08 (1H, d, *J*=7.9 Hz, H3), 7.82 (1H, t, *J*=7.9 Hz, H4), 7.61 (1H, d, *J*=7.9 Hz, H5), 7.27–7.38 (5H, m, arom. H), 5.44 (1H, dd, *J*=10.1, 8.8 Hz, H5′), 4.90 (1H, dd, *J*=10.2, 8.7 Hz, H5′), 4.70 (2H, s, CH_2), 4.39 (1H, t, *J*=8.6 Hz, H4′), 3.49 (3H, s, OCH_3). ^{13}C NMR δ 163.9, 159.2, 146.0, 141.9, 137.3, 128.8, 127.8, 126.9, 123.2, 123.0, 75.5, 75.3, 70.4, 58.9.

4.4. General procedure for the catalytic reaction

Ligand (0.029 mmol, 6 mol%) and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (3.5 mg, 0.0096 mmol, 2 mol%) were dissolved in dichloromethane (1 mL) under dry conditions. The solution was degassed at −78°C for 15 min. The vessel was sealed under nitrogen and the solution stirred at 50°C for 2 h. KOAc (2–3 mg, ~0.025 mmol, ~5 mol%), *N*,*O*-bis(trimethylsilyl)acetamide (292 mg, 1.44 mmol), dimethyl malonate (142 mg, 1.07 mmol), and 1,3-diphenyl-2-propenyl acetate (121 mg, 0.480 mmol) were transferred to the reaction vessel with dichloromethane (1 mL) at −78°C. After degassing as before the solution was stirred for 4 days under nitrogen at rt. Saturated aqueous NH_4Cl was added and the mixture was extracted with diethyl ether. The combined organic phases were dried ($MgSO_4$) and filtered, and the solvent was evaporated. Residual starting materials were removed with short path distillation. The ee was analyzed with ^{1}H NMR using Eu(hfc)$_3$ and/or HPLC using a chiral column: Daicel Chiralcel OD-H (0.46 cm ∅×25 cm), *n*-hexane:2-propanol (99:1), 0.5 mL/min as the mobile phase, UV-monitor (254 nm).

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