Highly Regio- and Enantioselective Palladium-Catalyzed Allylic Amination with Sodium Diformylamide

Yi Wang and Kuiling Ding*

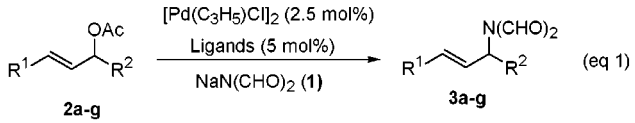
Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, P. R. China

kding@pub.sioc.ac.cn

Received February 2, 2001

Palladium-catalyzed asymmetric amination of allylic substrates for the preparation of enantiomerically enriched allylic amine derivatives has not been so well developed in comparison with allylic alkylation of carbon nucleophiles.[1] Although both secondary and tertiary allylic amines were obtained with excellent results through palladium-catalyzed amination,[2,3] primary allylic amines were difficult to obtain directly from nucleophilic substitution via ammonia. Therefore, the employment of "protected ammonia", such as phthalimide, *p*-toluenenesulfonamide, di-*tert*-butyl iminodicarbonate, methylcarbamate, or bis(trimethylsilyl)amides, was an alternative approach to afford allylic primary amines.[4] However, the application of the above reagents has been significantly limited by the difficulties of deprotection of amino group, reagent preparation, or low efficiency in terms of "atom economy".[5] Recently, sodium *N*,*N*-diformylamide (SDFA)[6] (**1**) was found to be an advanced alternative to classical Gabriel reagent for the preparation of primary amines,[7] having the advantages of easy availability, facile deprotection, and high atom economy. Nevertheless, its reaction with allylic acetate has not been developed. In this paper, we report the first highly regio- and enantioselective palladium-catalyzed amination of allylic acetates using **1** as a nucleophile.

The investigation was initiated by using 1,3-diphenylallylic acetate (**2a**) as substrate and dimeric allylpalladium chloride as catalyst precursor to test the reactivity of **1** and to find the matched ligands for the catalyst (eq 1). A variety of ligands ranging from monodentate PPh_3 to bidentate ligands, such as dppp (1,3-bis(diphenylphosphino)propane), dppb (1,4-bis(diphenylphosphino)butane, and dppf (1,1′- bis(diphenylphosphino)ferrocene), were examined for the reaction. It was obvious that the reactions catalyzed with PPh_3-, dppp-, and dppb-modified palladium complexes were sluggish in CH_3CN at 60 °C as shown in Table 1. On the contrary, dppf was found to be an excellent ligand. The conversion of **2** was completed in 3.5 h and *N*,*N*-diformalated 1,3-diphenylallylic amine (**3a**) could be isolated in 86% yield. Attention then was



2a: R^1 = Ph, R^2 = Ph	**3a**: R^1 = Ph, R^2 = Ph
2b: R^1 = H, R^2 = H	**3b**: R^1 = H, R^2 = H
2c: R^1 = Me, R^2 = Me	**3c**: R^1 = Me, R^2 = Me
2d: R^1 = Ph, R^2 = Me	**3d**: R^1 = Ph, R^2 = Me
2e: R^1-R^2 = -$CH_2CH_2CH_2$-	**3e**: R^1-R^2 = -$CH_2CH_2CH_2$-
2f: R^1 = Ph, R^2 = H	**3f**: R^1 = Ph, R^2 = H
2g: R^1 = H, R^2 = Ph	**3f**: R^1 = Ph, R^2 = H

* To whom correspondence should be addressed. Fax: 86-21-64166128.

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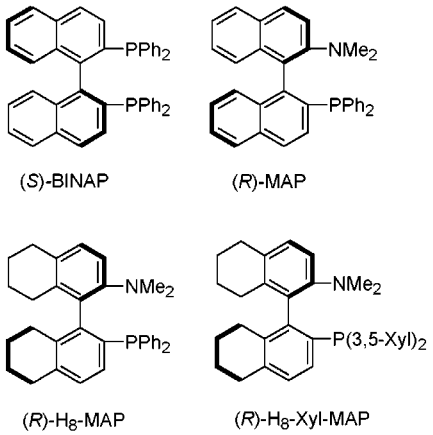
10.1021/jo015553m CCC: $20.00
Published on Web 04/07/2001

Table 1. Screening of Palladium Catalysts for Amination of Substituted Allylic Acetates with 1[a]

entry	ligand	allylic acetate	product	time (h)	yield[b] (%)
1	PPh_3c	**2a**	**3a**	12	18
2	dppp	**2a**	**3a**	12	trace
3	dppb	**2a**	**3a**	12	33
4	dppf	**2a**	**3a**	3.5	86
5	dppf	**2b**	**3b**	3.5	76
6	dppf	**2c**	**3c**	3.5	79
7	dppf	**2d**	**3d**	3.5	73
8	dppf	**2e**	**3e**	3.5	72
9	dppf	**2f**	**3f**	3.5	73
10	dppf	**2g**	**3f**	3.5	88

[a] All the reactions were carried out in CH_3CN at 60 °C with $[Pd(C_3H_5)Cl]_2$/ligand/**2**/**1** = 0.025:0.05:1:2. [b] Isolated yields. [c] Ligand was used at 10% mol.

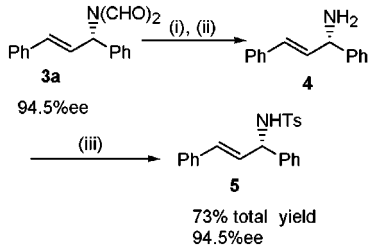
Scheme 1



turned to the scope of allylic acetate substrates (**2b**−**g**) and the regioselectivity of the reaction. All of the substrates examined including cyclic, linear, and branched allylic acetates underwent amination smoothly to give the corresponding *N*,*N*-diformyl allylic amines (**3b**−**f**) in good isolated yields (Table 1). In the case of allylic acetate **2d**, the reaction occurred at the carbon connected to methyl group exclusively (entry 7). Both 3-phenylallylic (**2f**) and 1-phenylallylic (**2g**) acetates gave only the linear 3-phenylallylic amine derivative (**3f**), supporting the nucleophiles attack from the less hindered side of the π-allylic palladium complex.

As an effort to develop the catalytic asymmetric version of this reaction, the P, P bidentate chiral ligand (*S*)-BINAP and N, P hybrid bidentate chiral ligands such as (*R*)-MAP, (*R*)-H_8-MAP, and (*R*)-H_8-Xyl-MAP (Scheme 1) were employed instead of dppf for asymmetric induction. As shown in Table 2, only a moderate level of enantioselectivity of the product was obtained with these ligands (entries 1−4). It seemed that MAP-type ligands showed better asymmetric induction than BINAP under the experimental conditions. Moreover, both partially reduced binaphthyl backbones and much bulkier aromatic rings at the phosphorus atom of MAPs were favorable to the improvement of reaction enantioselectivity (entry 2 vs 3 and 4). Nevertheless, the efficiency of the reaction with the catalysis of N, P ligand modified palladium complexes was low. Then we tried to improve the enantioselectivity of the reaction catalyzed by (*S*)-BINAP/Pd complex through alternating the reaction conditions. Indeed, decreasing the reaction temperature to 20 °C improved the enantioselectivity of the reaction significantly with moderate yield (entry 1 vs 5). The reaction

Scheme 2[a]



[a] Key: (i) 5% HCl/EtOH, reflux; (ii) 1 N aqueous NaOH, rt; (iii) TsCl, DMAP, Et_3N, CH_2Cl_2, rt.

solvent was also found to be critical for obtaining high-level enantioselectivity of the product. Excellent enantiomeric excesses (94.5−96.0%) of products could be obtained in less polar solvents, such as THF and toluene (entries 9−10). However, the yields were rather low probably because of poor solubility of **1** in these solvents. The enantioselectivity of the reaction in polar solvents, such as acetonitrile or 1,2-dichloroethane, could also be enhanced to the same level as in less polar solvents through further decreasing the reaction temperature to 0 °C and increasing the amount of nucleophile to 5 equiv simultaneously (entries 11−13). The interesting observation was that the yield of the reaction in 1,2-dichloroethane did not drop off upon lowering the reaction temperature (entry 6 vs 12). After several trials including adding a surfactant or tertiary amine, or raising the reaction temperature in less polar solvents to improve the efficiency of the reaction, it was found that the presence of Et_3N in the reaction system significantly enhanced the yield of product without any loss of enantioselectivity (entry 12 vs 14). Surprisingly, the employment of 6 equiv of nucleophile afforded almost quantitative yields after 6 h in the presence of 5 or even 1 equiv of Et_3N with a small decrease of enantioselectivity (entries 15 and 16). Further decreasing Et_3N to 0.5 equiv could slow the reaction even though the ee of product was slightly improved (entry 17).

The assignment of the absolute configuration of the product was accomplished by a two-step transformation of optically active **3a** to *N*-(1,3-diphenylallyl)-4-toluenesulfonamide (**5**), which possessed a known absolute configuration. Hydrolysis of **3a** in 5% HCl/EtOH resulted in the formation of hydrochloride of 1,3-diphenylallylamine (**4**). After treatment with 1 N aqueous NaOH, **4** underwent condensation with TsCl in the presence of Et_3N and 4-(dimethylamino)pyridine (DMAP) to give **5** in 73% total yield. Comparison of the specific optical rotation of **5** ($[\alpha]^{20}_D = 30.6$, $c = 0.5$, in $CHCl_3$) with that of known absolute configuration of the same compound[4d] confirmed that the absolute configuration of **3a** afforded with (*S*)-BINAP/Pd catalyst was *S*. Chiral HPLC analyses of **3a** and **5** showed that no racemization occurred during the transformation. Therefore, such a transformation also demonstrated a facile route for the preparation of optically active primary amine and a potential synthetic method for N-protected amino acid.[4g]

In conclusion, an advantageous amination reagent, sodium *N*,*N*-diformylamide, has been successfully applied in the palladium-catalyzed allylic amination. The catalytic asymmetric version has been also developed and excellent enantiomeric excess (93.9−96%) and yield (99%) of amination product have been achieved with the catalysis of (*S*)-BINAP/Pd by using 1,3-diphenylallylic

Table 2. Asymmetric Palladium-Catalyzed Amination of 2a with 1[a]

entry	ligand	solvent	**1** (equiv)	Et_3N (equiv)	*T* (°C)	time (h)	yield[b] (%)	ee[c] (%)
1	(*S*)-BINAP	CH_3CN	2		60	3.5	71	37.2 (*S*)
2	(*R*)-MAP	CH_3CN	2		60	12	14	45.7 (*R*)
3	(*R*)-H_8MAP	CH_3CN	2		60	60	7	60.9 (*R*)
4	(*R*)-H_8-Xyl-MAP	CH_3CN	2		60	60	4	68.8 (*R*)
5	(*S*)-BINAP	CH_3CN	2		20	24	59	87.2 (*S*)
6	(*S*)-BINAP	$ClCH_2CH_2Cl$	2		20	24	43	84.6 (*S*)
7	(*S*)-BINAP	DMF	2		20	24	33	86.2 (*S*)
8	(*S*)-BINAP	DMSO	2		20	24	65	31.3 (*S*)
9	(*S*)-BINAP	THF	2		20	24	18	94.5 (*S*)
10	(*S*)-BINAP	toluene	2		20	24	19	96.0 (*S*)
11	(*S*)-BINAP	CH_3CN	5		0	24	19	94.2 (*S*)
12	(*S*)-BINAP	$ClCH_2CH_2Cl$	5		0	24	43	94.5 (*S*)
13	(*S*)-BINAP	DMF	5		0	24	trace	93.0 (*S*)
14	(*S*)-BINAP	$ClCH_2CH_2Cl$	5	5	0	24	80	95.5 (*S*)
15	(*S*)-BINAP	$ClCH_2CH_2Cl$	6	5	0	6	97	93.9 (*S*)
16	(*S*)-BINAP	$ClCH_2CH_2Cl$	6	1	0	6	99	93.9 (*S*)
17	(*S*)-BINAP	$ClCH_2CH_2Cl$	6	0.5	0	24	85	95.5 (*S*)

[a] $[Pd(C_3H_5)Cl]_2$/ligand/allylic acetate = 0.025:0.05:1, the molar ratio of **1** to allylic acetate ranges from 2:1 to 6:1. [b] Isolated yield. [c] Determined with HPLC on Chiralcel AD column (hexane/2-propanol = 97:3, flow rate = 0.8 mL/min, t_S = 47.6 min, t_R = 50.6 min).

acetate as substrate. The screening and optimization of reaction conditions and matched catalyst systems for other substrates and the application of this amination reagent to other catalytic systems are currently under investigation.

Experimental Section

General and Materials. ^1H NMR was recorded in $CDCl_3$ on a Bruker AM300 at 20 °C, and the chemical shifts were expressed in ppm with TMS as an internal standard ($\delta = 0$ ppm). Optical rotation was measured with a PE−341 automatic polarimeter. Liquid chromatographic analyses were conducted on a JASCO 1580 system. EI Mass spectra were obtained on a HP5989A spectrometer. Elemental analysis was performed with an Elemental VARIO EL apparatus. All the experiments sensitive to moisture or air were carried out under argon atmosphere using standard Schlenk techniques. Optically pure MAP, H_8-MAP, and 3,5-di-xyl-H_8-MAP were prepared according to literature procedures.[8] All the allylic acetates were obtained by the reaction of corresponding allylic alcohol with acetic anhydride with the catalysis by DMAP. Other commercial available reagents were used as received without further purification unless otherwise noted. 1,2-Dichloroethane, DMSO, CH_3CN, and DMF were freshly distilled from calcium hydride, and toluene and THF were freshly distilled from sodium benzophenone ketyl.

Sodium Diformylamide (1).[6] A mixture of formamide (90 g, 2 mol) and sodium methoxide (54 g, 1 mol) was stirred at room temperature for 2.5 h under a dry atmosphere (drying tube). The flask was then evacuated and the temperature of the mixture gradually raised to 80 °C within 1.5 h. Stirring was continued at 80 °C for 1.5 h, and the mixture then was allowed to cool. The precipitated product **1** was isolated by suction and washed with THF: yield 91 g (96%).

***N,N*-Diformyl-1,3-diphenylprop-2-en-1-ylamide (3a).** To a Schlenk tube containing $[Pd(C_3H_5)Cl]_2$ (2.0 mg, 0.0056 mmol, 2.5 mol %) and dppf (6.2 mg, 0.0112 mmol, 5 mol %) was added dried CH_3CN (2 mL), and the mixture was stirred at room temperature for 10 min. Then 1,3-diphenylprop-2-en-1-yl acetate **2a** (56.4 mg, 0.224 mmol) was added, and the mixture was stirred for an additional 10 min. After being warmed to 60 °C and charged with sodium diformylamide (25.5 mg, 0.269 mmol, 120 mol %), the reaction mixture was allowed to stir at 60 °C for 3.5 h. After being cooled to room temperature, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was submitted to flash chromatography on silica gel with hexane/EtOAc (4:1) as eluent to produce **3a** as colorless oil (50.8 mg, 86%): ^1H NMR δ 6.25 (d, J = 3.7 Hz, 1H), 6.56−6.69 (m, 1H), 6.95 (br, 1H), 7.25−7.44 (m, 10H), 8.86 (s, 2H); EIMS *m*/*z* 265 ($[M]^+$, 34). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.71; H, 5.45; N, 5.11.

***N,N*-Diformylpropenyl amide (3b).**[7b] The same procedure for the preparation of **3a** was followed, except that 2 equiv of sodium diformylamide was used and the concentrated residue was submitted to flash chromatography on silica gel with light petroleum ether/Et_2O (1:1) as eluent to produce **3b** as colorless oil (76%, yield): ^1H NMR δ 4.25 (d, J = 5.7 Hz, 2H), 5.20−5.28 (m, 2H), 5.73−5.84 (m, 1H), 8.89 (s, 2H); EIMS *m*/*z* 114 ($[M + 1]^+$, 39).

***N,N*-Diformyl-1,3-dimethylprop-2-en-1-ylamide (3c).** The procedure for the preparation of **3a** was followed, except that 2 equiv of sodium diformylamide was used and the concentrated residue was submitted to flash chromatography on silica gel with light petroleum ether/Et_2O (2:1) as eluent to produce **3c** as colorless oil (79%, yield): ^1H NMR δ 1.42−1.45 (m, 3H), 1.63−1.69 (m, 3H), 4.95−4.99 (m, 1H), 5.30−5.72 (m, 2H), 8.78 (s, 2H); EIMS *m*/*z* 141 ($[M]^+$, 15); HRMS (EI) *m*/*z* calcd for $C_7H_{11}NO_2$ (M^+) 141.0790, found 141.0764. Anal. Calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.86; N, 9.92. Found: C, 58.90; H, 7.94; N, 10.16.

***N,N*-Diformyl-3-phenyl-1-methyl-prop-2-en-1-ylamide (3d).** The procedure for the preparation of **3a** was followed, except that 2 equiv of sodium diformylamide was used. **3d** was obtained as colorless oil (73%, yield): ^1H NMR δ 1.56 (d, J = 7.0 Hz, 3H), 5.17−5.21 (m, 1H), 6.55−6.60 (br, 2H), 7.24−7.38 (m, 5H), 8.86 (s, 2H); EIMS *m*/*z* 203 ($[M]^+$, 35). Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 71.12; H, 6.36; N, 6.70.

***N,N*-diformylcyclohex-2-en-1-ylamide (3e).** The procedure for the preparation of **3a** was followed, except that 2 equiv of sodium diformylamide was used and the concentrated residue was submitted to flash chromatography on silica gel with light petroleum ether/Et_2O (1:1) as eluent to produce **3e** as colorless oil (72%, yield): ^1H NMR δ 1.73−2.10 (br, 6H), 4.94 (br, 1H), 5.46−5.47 (m, 1H), 6.00 (br, 1H), 8.88 (s, 2H); EIMS *m*/*z* 153 ($[M]^+$, 6). Anal. Calcd for $C_8H_{11}NO_2$: C, 62.93; H, 7.24; N, 9.14. Found: C, 63.39; H, 7.28; N, 8.93.

***N,N*-Diformyl-3-phenylprop-2-en-1-ylamide (3f).** The procedure for the preparation of **3a** was followed, except that 2 equiv sodium diformylamide was used and the concentrated residue was submitted to flash chromatography on silica gel with hexane/EtOAc (2:1) as eluent to produce **3f** as crystalline solid (yields: 73% from **2f**, 88% from **2g**): ^1H NMR δ 4.38 (d, J = 6.5 Hz, 2H), 6.15 (dt, J = 6.8, 15.8 Hz, 1H), 6.64 (d, J = 15.8 Hz, 1H), 7.22−7.37 (m, 5H), 8.87 (s, 2H); EIMS *m*/*z* 189 ($[M]^+$, 31). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.82; H, 5.84; N, 7.30.

Typical Procedure for Palladium-Catalyzed Asymmetric Allylic Amination of 1,3-Diphenylprop-2-en-1-yl Acetate with Sodium Diformylamide. To a Schlenk tube containing $[Pd(C_3H_5)Cl]_2$ (1.7 mg, 0.0047 mmol, 2.5 mol %) and (*S*)-BINAP (6.7 mg, 0.0112 mmol, 6 mol %) was added 3 mL of

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$ClCH_2CH_2Cl$, and the mixture was stirred at room temperature for 10 min. Then 1,3-diphenylprop-2-en-l-yl acetate **2a** (46.8 mg, 0.186 mmol) and Et_3N (26 μL, 0.186 mmol, 100 mol %) were added, and the mixture was stirred for an additional 10 min. After the mixture was cooled to 0 °C, sodium diformylamide (106 mg, 1.116 mmol, 600 mol %) was added. The reaction mixture was allowed to stir at 0 °C for 6 h and filtered, and the concentrated filtrate was submitted to flash chromatography on silica gel with hexane/EtOAc (4:1) as eluent to produce (*S*)-**3a** as colorless oil (49.0 mg, 99%). The enantiomeric excess was determined by HPLC analysis on Chiralcel AD (hexane/*i*-PrOH = 97/3, 0.8 mL/min) to be 93.9%: $[\alpha]^{20}_D = -13.0$ (*c* 0.57, $CHCl_3$).

Assignment of the Absolute Configuration of *N,N*-Diformyl-1,3-diphenylprop-2-en-1-ylamide (3a). Optically active **3a** (20.3 mg, 0.077 mmol, 94.5% ee) was added into 5% HCl/EtOH (1 mL), refluxed overnight, cooled to room temperature, and neutralized with 1 N aqueous NaOH (2 mL). Then the mixture was extracted with Et_2O (2 × 20 mL), and the organic phase was washed with saturated brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to furnish **4**. The residue was charged with TsCl (17.6 mg, 0.092 mmol), Et_3N (15 μL), and DMAP (5 mol %) at room temperature in CH_2Cl_2 (1 mL). After being stirred for 8 h, the reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with saturated brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was submitted to flash chromatography on silica gel with hexane/EtOAc (4:1) as eluent to produce (*S*)-**5** as crystalline solid (20.2 mg, 73%). The enantiomeric excess was determined by HPLC analysis on a Chiralcel OD column (250 mm × 46ϕ mm, hexane/*i*-PrOH = 85/15, 0.7 mL/min, $t_R = 18.7$ min, $t_S = 26.1$ min) to be 94.5%: $[\alpha]^{20}_D = +30.6$ (*c* 0.5, $CHCl_3$); ^{1}H NMR δ 2.31(s, 3H), 5.10−5.15 (m, 2H), 6.07 (dd, J = 6.2, 15.8 Hz, 1H), 6.34 (d, J = 15.8 Hz, 1H), 7.12−7.29 (m, 12H), 7.66 (d, J = 8.4 Hz, 2H). Comparison of the optical rotation data with that reported[4d] confirmed the absolute configuration of the product to be *S*.

Acknowledgment. This work was financially supported by the Major Basic Research Development Program of China (Grant no. G2000077506), National Natural Science Foundation of China, Chinese Academy of Science, and the Science and Technology Commission of Shanghai Municipality.

JO015553M