Asymmetric Hydrogenation of Geminal-Substituted Vinyl Acetates

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1,1,1-Trifluoro-2-(acetyloxy)-2-propene was asymmetrically hydrogenated in high enantiomeric excess with [Rh(1,5-c-Oct)((*R*,*R*)-diPAMP)]$^+BF_4^-$ (1,5-c-Oct = 1,5-cyclooctadiene). This is the first vinyl acetate or vinylamide with a fully saturated substituent gem to the heteroatom which efficiently hydrogenates in high enantiomeric excess with any asymmetric catalyst. This result coupled with the hydrogenation data obtained from other chelating vinyl acetates clearly shows the need for an electron-withdrawing functionality gem to the acetoxy group, in addition to the olefin being able to chelate, in order to obtain high enantiomeric excesses with diPAMP (1).

Investigation into the catalytic asymmetric hydrogenation of prochiral olefins with rhodium(I) chiral phosphine complexes has burgeoned in the last 7 years, yielding numerous catalyst systems, some of which are shown in Figure 1, which can reduce (*Z*)-α-(acylamino)acrylic acids such as α-acetamidoacrylic acid (**7a**) rapidly in high (>85%) enantiomeric excesses (ee).[2] More recently the rhodium complex of diPAMP (1) has reduced itaconic acid derivatives[3a] such as the dimethyl ester (**7b**) and α-(acetyloxy)acrylic acid (**7c**)[3b] efficiently and in high enantiomeric excesses. The success of these three classes of substrates has been attributed primarily to their ability to chelate with the rhodium catalyst via the olefin and the carbonyl "tie down"[3-5] (Figure 2). According to spectrometric studies, the carbonyl group in amides and esters binds more strongly to rhodium than does that of simple olefins. This indicates that the olefin probably coordinates after the carbonyl group on "tie down", and the substituents on the other positions of the olefin determine which face can bind more easily. Because of the "face/edge" array of the phenyl groups on the rhodium complex of diPAMP the trans position to the tie down must be a hydrogen for efficient hydrogenations while the cis position can be virtually any alkyl or aryl group.[7,8] The role of the functionality gem to the tie down, however, has been studied in much less detail and has always been an unsaturated group such as a carboxylic acid, ester, or amide. We would like to (a) report the first example of a chelating olefin with a fully saturated geminal substituent to hydrogenate rapidly and with high enantiomeric excess, (b) illustrate the importance of the geminal functionality being strongly electron withdrawing, and (c) broaden the applicability of asymmetric hydrogenation.

Results and Discussion

An unsaturated geminal functionality has always been present in the chelating substrates which have been hydrogenated in high enantiomeric excesses. The role of this unsaturated group has been attributed to its ability to (a) be planar with the olefin, lie parallel to the face of the aryl ring on the ligand, and reduce unwanted steric repulsions when the re face is coordinated, (b) have a π–π interaction with the aryl group on the ligand which would help form a tighter catalyst/substrate complex for the re face, or (c) make the olefin more electropositive, which would have the same effect as the π–π interactions. To help understand which of these effects are important the asymmetric hydrogenation of 1,1,1-trifluoro-2-(acetyloxy)-2-propene was investigated. This substrate was ideal because the geminal functionality was sterically large, was strongly electron withdrawing, and lacked unsaturation. Surprisingly, the rhodium complex of diPAMP (1) reduces it efficiently and at a rate comparable to olefins **7a** and **7c** (Table I). This result gives a lot of credence to the need for an electropositive olefin. To determine if this was a universal phenomenon, we investigated other catalysts which were known to reduce (*Z*)-α-(acylamino)acrylic acids in high enantiomeric excesses. Each one appeared to give low enantiomeric excesses and at rates much less than the diPAMP (1) catalyst.[10] These results have not been optimized as to temperature or solvent, but it is very unlikely that the results would change considerably. In order to eliminate simple steric interactions and to lend further credibility to the importance of the electron-withdrawing effect as the role of the geminal functionality, we asymmetrically hydrogenated three representative para-substituted 1-phenyl-1-(acetyloxy)ethylenes (Table II). Even though the enantiomeric excesses are similar, they are in direct relationship with the electron-withdrawing ability of the para substituent (NO_2 > H > OCH_3). This lends further support to the hypothesis that in addition to the prochiral olefin being able to chelate to the catalyst, it must also have a geminal functionality which is electron withdrawing in order to hydrogenate efficiently and in high enantiomeric excesses with the Rh(I) complex of diPAMP (1). Because of the large variation between the catalyst systems (Table I) for the asymmetric reduction of 1,1,1-trifluoro-2-(acetyloxy)-2-propene, it was important to determine if this was a general phenomenon of the acetoxy tie down or simply limited to this unusual example. Hence a study employing the reaction conditions most widely used by other investigators and with a traditional sub-

(1) (a) Monsanto Corporate Research Laboratories. (b) Monsanto Industrial Chemicals Co.

(2) Valentine, D.; Scott, J. W. *Synthesis* **1978**, 329-56.

(3) (a) Christopfel, W. C.; Vineyard, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 4406-8. (b) B. D. Vineyard and G. L. Bachman, U.S. Patent.

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(5) (a) Halpern, J. *Trans. Am. Crystallogr. Assoc.* **1978**, *14*, 59. (b) Brown, J. M.; Chaloner, P. A. *J. Chem. Soc., Chem. Commun.* **1978**, 321. (c) Brown, J. M.; Chaloner, P. A.; Descotes, G.; Glaser, R.; Lafont, D.; Sinou, D. *Ibid.* **1979**, 611. (d) Brown, J. M.; Chaloner, P. A. *Ibid.* **1979**, 613.

(6) A detailed study with chiraphos (2) and prophos (3) on the synthesis of labeled α-(acetyloxy)propionic acid asymmetric hydrogenation was reported: Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1978**, *100*, 3491.

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(10) Rates are very hard to reproduce accurately at low catalyst concentrations because trace amounts of poisons in the solvent or substrate can easily kill a high percentage of active catalyst. However, if hydrogenation occurs, the enantiomeric excesses obtained seem to be independent of poisons or the counterion of the catalyst.

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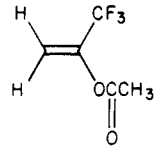
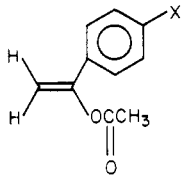
Table I. Asymmetric Hydrogenation of 1,1,1-Trifluoro-2-(acetyloxy)-2-propene[a]



ligand (amt, mg)	amt of substr, g	reactn time, h	reactn temp, °C	% completion	enantiomeric excess[d]	config
(*R,R*)-diPAMP (18.2)	0.64	*b*	24	100	70	*S*
(22.6)	0.62	*b*	50	100	77	*S*
(15.2)	0.59	0.25	77	100	69	*S*
(*S,S*)-chiraphos (13.0)	0.62	*b*	50	79[c]	38	*R*
(*R*)-CAMP (14.4)	0.61	2.0	50	100	28	*S*
(*S,S*)-BPPM (15.6)	0.59	3.5	44	40[c]	10	*S*
(*R,R*)-DIOP (13.4)	0.53	30	50	30[c]	0	

[a] All reactions were run at 50 psig in methanol. [b] Reactions were not monitored and were allowed to react overnight. [c] The balance is unreacted starting material. [d] Obtained by a chiral shift study with tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium(III).

Table II. Asymmetric Hydrogenation of Para-Substituted 1-Phenyl-(acetyloxy)ethenes[a]



X	amt of substr, g	amt of (*R,R*)-diPAMP, mg	solvent	reactn time, h	% completion	enantiomeric excess[b]
NO_2	0.5	21.0	MeOH	0.75	100	65
H	2.6	19.5	EtOH	1.0	100	55
OCH_3	0.7	27.7	MeOH	1.25	70[c]	51

[a] All hydrogenations run at 50 °C and 50 psig. [b] Obtained by a chiral shift reagent study with tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium(III). [c] Approximately 30% hydrogenolysis products were observed.

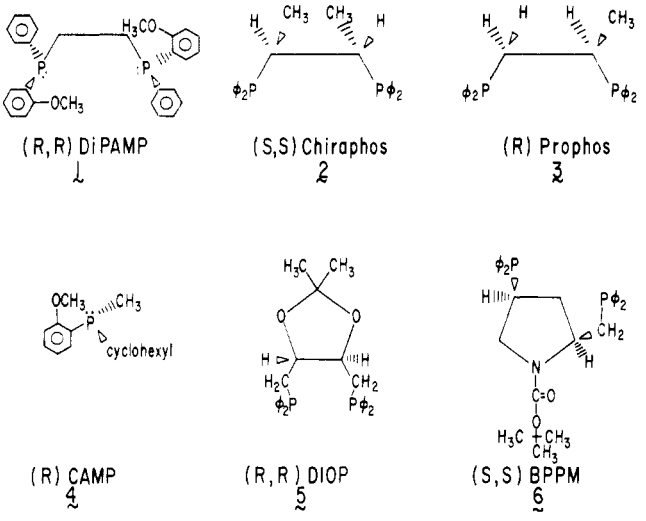


Figure 1. Ligand systems.

strate, α-(acetyloxy)acrylic acid, was undertaken (Table III). Even though each of the catalyst systems works well with (*Z*)-α-(acylamino)acrylic acids (the amide analogue), the corresponding acetoxy system gave varying results. The rhodium complex of diPAMP (1) appears to give the most consistent results regardless of the chelating system used, at least in protic solvents.

Conclusions

We have (1) found the first chelating olefin with a fully saturated geminal functionality [1,1,1-trifluoro-2-(acetyloxy)-2-propene] to hydrogenate in good enantiomeric excess, (2) demonstrated the role of the geminal substituent to be clearly electron withdrawing in chelating olefins, and (3) broadened the applications for asymmetric hydrogenation catalysis as well as defined its limitations with the present catalyst systems.

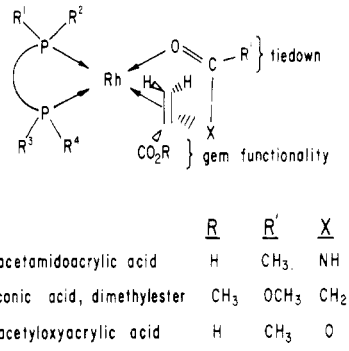
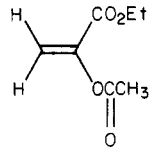


Figure 2.

Experimental Section

NMR spectra were obtained on a Varian EM-390 or a Varian T-60 and refer to ~15% solutions in $CDCl_3$ or CCl_4 with tetramethylsilane as an internal reference. The para-substituted 1-phenyl-1-(acetyloxy)ethylenes were obtained by refluxing the corresponding substituted acetophenones in acetic anhydride in the presence of a catalytic amount of *p*-toluenesulfonic acid and were purified by distillation. 1,1,1-Trifluoro-2-(acetyloxy)-2-propene was purchased from Aldrich, and DIOP (5) was obtained from Strem Chemicals, Inc. Commercial-grade solvents were used without purification except for THF, which was freshly distilled from sodium ketyl. All hydrogenations were conducted at 50 psig

Table III. Asymmetric Hydrogenation of Ethyl 2-(Acetyloxy)-2-propenoate



ligand (amt, mg)	amt of substr, g	solvent	reactn time, h	reactn temp, °C	pressure	% completion	enantiomeric excess[a]	config
(*R,R*)-diPAMP (18.7)	2.0	EtOH	0.4	50	50 psig	100	89	*S*
(*S,S*)-chiraphos		THF		25	1 atm		84[b,d]	*R*
(*R*)-prophos (150)	10.7	THF	5.5	25	1 atm	91[e]	81[b]	S
(*S,S*)-BPPM (13.0)	0.5	EtOH	0.6	50	50 psig	100	67	*R*
(*R*)-CAMP (20.2)	1.2	EtOH	0.3	50	50 psig	100	52	*S*
(*R,R*)-DIOP (6.6)	1.0	EtOH	*c*	50	50 psig	93	27	*R*

[a] Based on $[\alpha]^{20}_D$ 50.3° (*c* 0.99, $CHCl_3$) for the pure material.[6] [b] Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1978**, *100*, 3491. [c] Reaction was not monitored and was allowed to react overnight. [d] When conditions were the same as for diPAMP, a 57% ee (*R* configuration) was obtained. [e] Distilled yield.

of hydrogen and 50 °C unless otherwise noted.

Catalyst Formation. (1,5-Cyclooctadiene)bis[(*R*)-cyclohexyl(*o*-methoxyphenyl)methylphosphine]rhodium Tetrafluoroborate. To a 1-L flask purged with N_2 was added 300 mL of methanol and 15.4 g (0.031 mol) of $[Rh(c\text{-}Oct)Cl]_2$, making a thin slurry. Then 30.3 g (0.12 mol, assay 98%) of CAMP (4)[9] was added and the mixture stirred 0.5 h to give a red-orange solution. A solution of sodium tetrafluoroborate (13.7 g, 0.12 mol) in 160 mL of water was added over 1 h. Orange crystals separate, and they were collected and washed with two 30-mL portions of water. The product, dried in vacuo at 25 °C, weighed 45 g (95%); mp 170–175 °C dec. This material was about 96% optically pure and gave a 77.5% enantiomeric excess (ee) on hydrogenation with (*Z*)-α-(acetamido)cinnamic acid at 25 °C and 40 psig of H_2 in methanol. Recrystallized from ethanol, the catalyst gave an ee as high 80.5%.

(1,5-Cyclooctadiene)[(*R,R*)-1,2-ethanediylbis(*o*-methoxyphenyl)phenylphosphine]rhodium Tetrafluoroborate. A slurry of 1.83 g (4.0 mmol) of 1[4] was added to 12 mL of 90% methanol. Then, under nitrogen at 25–30 °C, 0.99 g (2.0 mmol) of $[Rh(1,5\text{-}c\text{-}Oct)Cl]_2$ was added. The slurry became orange and after being stirred for 1 h gave a red-orange solution. The complex was precipitated by slowly adding a solution of 0.66 g (6.0 mmol) of sodium tetrafluoroborate in 5 mL of H_2O over 2 h. After 1 h of stirring at 25 °C, the fine crystals were filtered, washed twice with 3-mL portions of water, and dried at 25 °C (5 mm). (1,5-Cyclooctadiene)[(*R,R*)-1,2-ethanediylbis(*o*-methoxyphenyl)-phenylphosphine]rhodium tetrafluoroborate (2.8 g, 90%) was obtained. If necessary, the product may be purified by crystallization from absolute EtOH. Its purity is best measured by its catalytic efficiency. [(*Z*)-α-Acetamidocinnamic acid hydrogenates to give 94.0% ee at 50 °C and 3 atm of H_2.]

Bis[(2,3-*O*-isopropylidene)[2,3-dihydroxy-1,4-bis(diphenylphosphino)butane]rhodium] Dichloride. In a flame-dried, nitrogen-purged, 250-mL, round-bottomed flask was placed 285 mg (0.618 mmol) of bis[(norbornadiene)rhodium] dichloride in 20 mL of deoxygenated methanol. After the mixture stirred for 5 min, 650 mg (1.30 mmol) of (-)-DIOP (5) dissolved in 30 mL of hot deoxygenated ethanol (100%) was added in one portion. The solution immediately became red and homogeneous. After the mixture stirred for 5 min, a solution of 468 mg (1.37 mmol) of sodium tetraphenylborate in 20 mL of deoxygenated ethanol (100%) was added in one portion. Yellow crystals appeared immediately and after 15 min of additional stirring were filtered, rinsed with ether, and dried at 25 °C (1 mm) for 14 h (1.15 g, 92% yield). Its purity was measured by its catalytic efficiency [(*Z*)-α-acetamidocinnamic acid was hydrogenated in 88% isopropyl alcohol to give $[\alpha]_D^{20}$ -42.8° which indicates 72.2% ee; hence it was 94% optically pure].

(1,5-Cyclooctadiene)[(-)-(*S,S*)-2,3-bis(diphenylphosphino)butane]rhodium Acetylacetonate. In 0.5 mL of deoxygenated methanol was placed 8.1 mg (2.6×10^{-2} mmol) of Rh(1,5-c-Oct)(acac). Nitrogen was bubbled through the suspension for 2 min, (*S,S*)-chiraphos (2; 10.7 mg, 2.5×10^{-2} mmol) in 0.5 mL of deoxygenated methanol was added, and nitrogen bubbling was continued until the solution became homogeneous. This solution was then injected into the hydrogenation bottle without further purification.

(1,5-Cyclooctadiene)[(2*S*,4*S*)-*N*-(butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]-pyrrolidine]rhodium Acetylacetonate. In 0.5 mL of deoxygenated methanol was placed 5.6 mg (1.8×10^{-2} mmol) of Rh-(1,5-c-Oct)(acac). Nitrogen was bubbled through the suspension for 2 min, (*S,S*)-BPPM (6; 10 mg, 1.8×10^{2} mmol) in 0.5 mL of deoxygenated methanol was added, and nitrogen bubbling was continued until the solution was homogeneous. This solution was then injected into the hydrogenation bottle without further purification.

Typical Hydrogenation of 1,1,1-Trifluoro-2-(acetyloxy)-2-propene. Ethanol was thoroughly deoxygenated by bubbling dry nitrogen through the solution for 10 min immediately prior to use. 1,1,1-Trifluoro-2-(acetyloxy)-2-propene (0.62 g, 4.0 mmol) and 20 mL of deoxygenated ethanol were placed in a 90-mL glass hydrogenation bottle containing a magnetic stirring bar. The mixture was immediately evacuated and then charged with nitrogen to 30 psig. This procedure was repeated 8–10 times. The bottle was then heated to 50 °C and pressurized with hydrogen to 50 psig. The catalyst solution was then injected via a septum. The completion of the hydrogenation was monitored by hydrogen uptake. Upon completion, the reaction media was cooled to room temperature, and 3 mL of CCl_4 and 90 mL of water (saturated with NaCl) were added. The organic layer was separated, washed with an additional 50 mL of water (saturated with NaCl), and dried with $MgSO_4$. The asymmetric induction was measured in CCl_4 by a chiral shift study with tris[3-[(heptafluoropropyl)-hydroxymethylene]-*d*-camphorato]europium(III). The methyl group on the acetyl was monitored and base-line separation of the enantiomers was obtained at a $\Delta\delta$ of ~1.9–2.2.

Hydrogenation of Ethyl 2-(Acetyloxy)-2-propenoate. The hydrogenation was conducted in exactly the same way as in the preceding example. Upon completion, the reaction vessel was cooled to room temperature. Either the reduced material was isolated directly by distillation or the catalyst was removed by ion-exchange chromatography by placing the reaction solution through prefilled Bio-Rad Econo-Columns (AG 50W-X8) until colorless followed by removal of the solvent under reduced pressure. A rotation was then obtained, and the optical purities were based on $[\alpha]^{20}_D$ 50.3° (*c* 1.0, $CHCl_3$) for the pure material.

Hydrogenation of Para-Substituted 1-Phenyl-1-(acetyloxy)ethenes. The hydrogenation was conducted in exactly the same fashion as in the 1,1,1-trifluoro-2-(acetyloxy)-2-propene case. Upon completion the reaction vessel was cooled to room temperature. The hydrogenated compound was isolated by distillation. The asymmetric induction was measured in $CDCl_3$ by chiral shift studies with tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium(III). The methyl group on the acetyl was monitored in each case, and base-line separation of the enantiomers was obtained at a $\Delta\delta$ of 0.23 for 1-(*p*-meth-

oxylphenyl)-1-(acetyloxy)ethene, 0.12 for 1-phenyl-1-(acetyloxy)ethene, and 0.10 for 1-(*p*-nitrophenyl)-1-(acetyloxy)ethene.

Acknowledgment. We warmly thank Dr. B. Bosnich and Dr. Kazuo Achiwa for their generous gift of (*S,S*)-chiraphos and (*S,S*)-BPPM, respectively. We also greatly appreciate the open and candid communications we have had with many investigators in the area of asymmetric hydrogenations, especially Dr. Kazuo Achiwa, Dr. B. Bosnich, Dr. John Brown, Dr. Jack Halpern, Dr. B. R. James, Dr. Henri Kagan, and Dr. Iwao Ojima.

Registry No. 1, 55739-58-7; 2, 64896-28-2; 3, 67884-32-6; 4, 52885-02-6; 5, 32305-98-9; 6, 61478-28-2; (1,5-cyclooctadiene)bis[(*R*)-cyclohexyl(*o*-methoxyphenyl)methylphosphine]rhodium tetrafluoroborate, 65375-70-4; $[Rh(c\text{-}Oct)Cl]_2$, 12092-47-6; (1,5-cyclooctadiene)[(*R,R*)-1,2-ethanediylbis(*o*-methoxyphenyl)phenylphosphine]rhodium tetrafluoroborate, 71423-54-6; bis[(*R,R*)-2,3-*O*-isopropylidene][2,3-dihydroxy-1,4-bis(diphenylphosphino)butane]-rhodium dichloride, 63569-12-0; bis[(norbornadiene)rhodium] dichloride, 12257-42-0; (1,5-cyclooctadiene)[(−)-(*S,S*)-1,4-bis(diphenylphosphino)butane]rhodium acetylacetonate, 73173-81-6; Rh(1,5-c-Oct)(acac), 12245-39-5; (1,5-cyclooctadiene)[(2*S*,4*S*)-*N*-(butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)-methyl]pyrrolidine]rhodium acetylacetonate, 73173-82-7; 1,1,1-trifluoro-2-(acetyloxy)-2-propene, 2247-91-8; ethyl 2-(acetyloxy)-2-propenoate, 22807-79-0; 1-(*p*-methoxyphenyl)-1-(acetyloxy)ethene, 22390-98-3; 1-phenyl-1-(acetyloxy)ethene, 2206-94-2; 1-(*p*-nitrophenyl)-1-(acetyloxy)ethene, 22391-01-1; (*S*)-1,1,1-trifluoro-2-(acetyloxy)propane, 73208-27-2; (*R*)-1,1,1-trifluoro-2-(acetyloxy)propane, 73208-28-3; 1-(*p*-nitrophenyl)-1-(acetyloxy)ethane, 19759-27-4; 1-phenyl-1-(acetyloxy)ethane, 93-92-5; 1-(*p*-methoxyphenyl)-1-(acetyloxy)ethane, 945-89-1; ethyl (*S*)-2-(acetyloxy)propanoate, 20918-91-6; ethyl (*R*)-2-(acetyloxy)propanoate, 20918-92-7; (±)-1-(*p*-nitrophenyl)-1-(acetyloxy)ethane, 73104-87-7; (±)-1-phenyl-1-(acetyloxy)ethane, 50373-55-2; (±)-1-(*p*-methoxyphenyl)-1-(acetyloxy)-ethane, 73104-88-8.

Reaction of Diazonium Salts with Transition Metals. 4. Palladium(0)-Catalyzed Carboxylation of Arenediazonium Salts[1]

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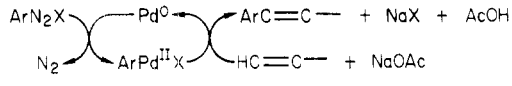
Various arylamines were converted to arenecarboxylic acids in good yields via their diazonium tetrafluoroborates by reaction with carbon monoxide (9 kg/cm^2) in the presence of a palladium(0) catalyst and sodium acetate. Evidence is presented which supports the idea that mixed anhydrides are initial products in the carboxylation.

Previous papers[1,2] described that in the presence of a palladium(0) catalyst and sodium acetate, arenediazonium salts were conveniently utilized for the arylation of various olefins. The copper-catalyzed arylation by arenediazonium salts, the Meerwein arylation, generally requires activated olefins with electron-withdrawing groups to attain a comparable yield of arylated olefins.[3] In contrast, the palladium-catalyzed arylation can be applied to olefins bearing both electron-releasing and -withdrawing substituents.[1] The features of the reaction are reasonably interpreted by the intermediacy of an arylpalladium species and by the following catalytic cycle analogous to the palladium-catalyzed arylation by aryl halides.[4] The formation of aryl-



diazonatopalladium complexes or arylpalladium complexes in the treatment of arenediazonium salts with tetrakis(triphenylphosphine)palladium(0) further supports the proposed mechanism.[5] Carboalkoxylation of aryl halides via arylpalladium intermediates is well-known.[6] Therefore, it is to be expected that the arylpalladium species produced from arenediazonium salts might undergo reaction with carbon monoxide to give arenecarboxylic acid derivatives. This paper describes a convenient method for synthesizing various arenecarboxylic acids from diazonium salts under mild conditions and the formation of a mixed acid anhydride as an initial reaction product.

Table I. Effects of Reaction Conditions on Carboxylation of Benzenediazonium Tetrafluoroborate[a]

PhN_2BF_4, mmol	solvent[b] (mL)	catalyst (mol %)	reaction time, h	yield,[c] %
25	MC (150)	$Pd(dba)_2$ (4)	2	9
25	AC (150)	$Pd(dba)_2$ (4)	2	30
25	MC–AC (75/75)	$Pd(dba)_2$ (4)	2	58
25	AN (150)	$Pd(dba)_2$ (4)	2	77
25	AN (150)	Li_2PdCl_4 (4)	2	73
25	AN (150)	$Pd(OAc)_2$ (4)	2	85
25	AN (150)	$Pd(OAc)_2$ (4)	0.5	85
10	AN (60)	$Pd(OAc)_2$ (2)	1	83
10	AN (60)	$Pd(OAc)_2$ (1)	1	82
10	AN (60)	$Pd(OAc)_2$ (1)	1	71[d]

[a] Sodium acetate (3 mol) and 9 kg/cm^2 of carbon monoxide were used unless otherwise noted. [b] MC = methylene chloride, AC = acetone, and AN = acetonitrile. [c] Isolated yields based on PhN_2BF_4. [d] Atmospheric pressure of carbon monoxide was used.

Results and Discussion

An exothermic reaction was observed when a mixture of benzenediazonium tetrafluoroborate, a catalytic amount (2 mol %) of palladium acetate, and sodium acetate in acetonitrile was stirred under carbon monoxide pressure (9 kg/cm^2) at room temperature. The reaction mixture was hydrolyzed with aqueous sodium hydroxide. Acidi-

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