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-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 aryldiazonatopalladium 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.

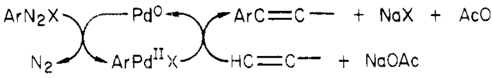

Table I. Effects of Reaction Conditions on Carboxylation of Benzenediazonium Tetrafluoroborate[a]

PhN$_2$-BF$_4$, 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$_2$PdCl$_4$ (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$_2$BF$_4$. [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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(1) Part III: K. Kikukawa, K. Nagira, F. Wada, and T. Matsuda, *Tetrahedron*, in press.

(2) K. Kikukawa and T. Matsuda, *Chem. Lett.*, 159 (1977); K. Kikukawa, N. Terao, K. Nagira, F. Wada, and T. Matsuda, *Bull. Chem. Soc. Jpn.*, **52** 2609 (1979).

(3) C. S. Rondestvest, Jr., *Org. React.*, **11**, 189 (1960); **24**, 225 (1977).

(4) R. F. Heck, *Pure Appl. Chem.*, **50**, 691 (1978); *Acc. Chem. Res.*, **12**, 146 (1979).

(5) K. Kikukawa, R. Yamashita, M. Takagi, and T. Matsuda, *Int. Conf. Organometal. Chem., Kyoto, 8th*, 1977, Abstract 253 (1977).

(6) A. Scheonberg, I. Bartoletti, and R. F. Heck, *J. Org. Chem.*, **39**, 3318 (1974).

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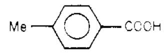
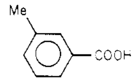
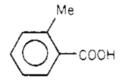
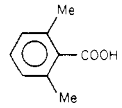
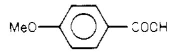
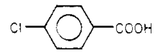
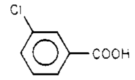
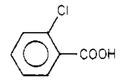
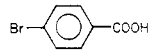
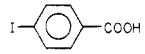
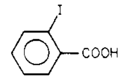
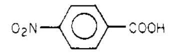
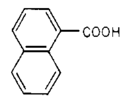
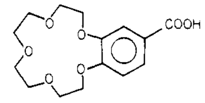
fication with hydrochloric acid and extraction of the mixture with ether gave almost pure benzoic acid. Examination of the reaction conditions summarized in Table I shows that the reaction can be completed within 0.5 h at room temperature and proceeds even in the presence of 1 mol % catalyst. Solvent effects were more significant than those in the olefin arylation, and acetonitrile gave good results in the carboxylation. Both zero and divalent palladium complexes could be used successfully. However, when bis(dibenzylideneacetone)palladium(0) (the best catalyst in the olefin arylation) was used, mixing of the reactants had to be done while cooling with a dry ice–methanol bath to avoid a spontaneous reaction of the catalyst with the diazonium salt. Some induction period (~0.5 h) was observed with lithium tetrachloropalladate. Thus, the use of palladium acetate was preferred to get reproducible results and also to simplify the reaction procedure.

Table II gives the results of the carboxylation of various arenediazonium salts in acetonitrile at room temperature under 9 kg/cm^2 of carbon monoxide pressure with 2 mol % palladium acetate. Both electron-withdrawing and -releasing substituents in the diazonium salts do not materially affect the yields. The successful preparation of *p*-nitrobenzoic acid is notable since the presence of a nitro group (para or ortho) on the aromatic ring causes a marked decrease of the yield in the olefin arylation. Halo groups did not enter into reactions such as carboxylation or reductive elimination. One of the important factors to get good and reproducible results is the suppression of formation of tarry materials, which markedly reduce activity of the catalyst. In order to do this, it is necessary to avoid contact of the diazonium salt with sodium acetate or to cool the reaction mixture (0 °C) until the atmosphere in the reaction vessel has been fully replaced by carbon monoxide. In acetonitrile, the diazonium salts react with sodium acetate with evolution of nitrogen and form a considerable amount of tarry materials, irrespective of the absence of the catalyst. Under an atmosphere of carbon monoxide, however, the decomposition markedly decreased. *p*-Iodobenzenediazonium salt gave an 86% yield of *p*-iodobenzoic acid in a 15-min reaction; the product was found to be contaminated with less than 0.1% of terephthalic acid by GLC examination after its conversion to the methyl ester with excess diazomethane. The selective formation of iodo- and bromobenzoic acids shows that the diazonium group enters into the reaction with greater ease than the carbon–iodine (or –bromine) bond, and the combination of arenediazonium salts and palladium(0) gives a convenient method to produce halo-substituted arylpalladium species.

The fair to excellent yields attained irrespective of the type of the substituent suggest the utility of the present carboxylation in synthetic organic chemistry in view of the fact that yields in the conventional conversion of diazonium salts to carboxylic acids via nitriles, the Sandmeyer reaction, are highly variable.

Table II. Carboxylation of Arenediazonium Tetrafluoroborates[a]

ArCOOH	yield, %[b]	mp, °C (lit. mp, °C)[c]
	84	178-180 (179-180)
	66	109-113 (110-111)
	68	103-104 (104-105)
	28[d]	112-114 (116)
	58	178-181 (184.2)
	79	236-241 (239.7)
	78	154-156 (154.3)
	82	140-142 (140.2)
	84	252-253 (251-253)
	86[e]	~260[f] (sublimed) (269-270)
	74	159-160 (162)
	65	240-242 (240-242)
	72	161-162 (161-163)
	28[g]	181-183 (179-181)[h]

[a] See general procedure in Experimental Section for reaction conditions. [b] Isolated yields based on ArN_2BF_4. All acids obtained here gave satisfactory IR spectra. [c] Unless otherwise noted melting points were cited from "Lange's Handbook of Chemistry", 11th ed., McGraw-Hill, New York, 1973. [d] 2,6-Dimethylbenzoic anhydride (3%) and aceto-2,6-dimethylanilide (16%) were also formed. [e] Reaction time was 15 min. [f] Melting point of methyl ester of the product was 113.5-115 °C (lit.[c] mp 114 °C). [g] The diazonium hexafluorophosphate was used. [h] M. Bourgoin, K. H. Wong, J. R. Hui, and J. Smid, *J. Am. Chem. Soc.*, 97, 3462 (1975).

Heck and co-workers[6] have successfully carried out palladium-catalyzed carboalkoxylations of aryl halides in the presence of alcohols. In the present systems, however, the presence of alcohols such as methanol and ethanol decreased the yield of carboxylated products and led to a mixture of acid and ester (Table III). The lower product yields could be attributable to reductive decomposition of the diazonium salt by the alcohols bearing α hydrogens to give arenes and/or alkoxy arenes.[7] The palladium catalyst may assist the side reaction in the following manner, in view of the fact that palladium(II) salts are easily reduced by alcohol in the presence of sodium acetate (eq 1).

$$ArN_2X + Pd^0 \rightarrow Ar\text{-}Pd\text{-}X \xrightarrow{NaOAc} Ar\text{-}Pd\text{-}OAc \xrightarrow{RCH_2OH} Ar\text{-}Pd\text{-}OCH_2R \rightarrow Ar\text{-}Pd\text{-}H\ (+\ RCHO) \rightarrow ArH + Pd^0 \quad (1)$$

Use of *tert*-butyl alcohol gave a considerable amount of benzoic anhydride together with a small amount of esters on distillation of the reaction mixture. No attempt was made to investigate the origin of the methyl benzoate. The formation of benzoic anhydride prompted us to examine the reaction mixture before hydrolysis. The infrared

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(7) N. Kornblum, *Org. React.*, 2, 262 (1944).

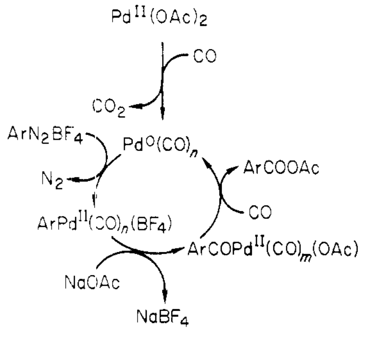
Table III. Attempted Carboalkoxylations of Benzenediazonium Tetrafluoroborate

PhN_2BF_4, mmol	alcohol (mL)	solvent[a] (mL)	catalyst (mol %)	product[b] (%)
25	MeOH (20)	MC-AC (75/75)	$Pd(dba)_2$ (2)	PhCOOH (7) PhCOOMe (16)
25	EtOH (30)	MC-AC (75/75)	$Pd(dba)_2$ (2)	PhCOOH (16) PhCOOEt (21)
25	*t*-BuOH (45)	MC-AC (75/75)	$Pd(dba)_2$ (2)	PhCOOH (25) PhCOOMe (2) PhCOO-*t*-Bu (3) $(PhCO)_2O$ (44)
10	*n*-BuOH (30)	AN (30)	$Pd(OAc)_2$ (2)	PhCOOH (29)[c] PhCOO-*n*-Bu (15)
10	*t*-BuOH (15)	AN (60)	$Pd(OAc)_2$ (2)	PhCOOH (66)[c] PhCOO-*t*-Bu (trace)

[a] See Table I. [b] The product distributions were determined by GLC as well as NMR analyses of distilled products except for benzoic acid. Yields are based on the diazonium salt used. The structures of each product were assigned by comparison with authentic specimens by GLC. [c] The reaction mixture was hydrolyzed with aqueous sodium hydroxide.

spectrum of the filtered reaction mixture obtained in the absence of alcohol showed two characteristic absorptions in the carbonyl region (1809 and 1740 cm^{-1}). Comparison with the IR spectra of acetic anhydride (1819 and 1758 cm^{-1}) and benzoic anhydride (1789 and 1725 cm^{-1}) in acetonitrile strongly suggested that the two absorptions could be assigned to acetic benzoic anhydride. When the reaction mixture was treated with excess aniline at room temperature, we obtained considerable amounts of acetanilide and benzoic acid (eq 2). Treatment of acetic benzoic anhydride with aniline is known to give a mixture of benzanilide (2%), acetanilide (83%) and benzoic acid (87%).[8] From these observations it is probable that the present reaction affords the mixed acid anhydride as an initial product, in which one of the acyl group comes from sodium acetate and the other from the diazonium salt; disproportionation by heat leads to benzoic anhydride (and acetic anhydride). The formation of the mixed anhydride and the role of sodium carboxylate are further supported by the fact that similar reaction of naphthalene-1-diazonium salt in the presence of sodium benzoate gave a 45% yield of benzoic 1-naphthoic anhydride (mp 85–91 °C, lit.[9] mp 89.5–90.3 °C). The following scheme can reasonably explain the present palladium-catalyzed carboxylation of arenediazonium salts. Aroylpalladium acetate, formed by ligand exchange in aroylpalladium tetrafluoroforate or carbon monoxide insertion to arylpalladium acetate, is supposed to undergo reductive elimination to give mixed anhydrides. However, one of the alternative routes to the anhydride, nucleophilic attack of acetate ion on the aroylpalladium complex, cannot be entirely excluded at the present stage since there are several observations of the attack of a nucleophile (ions such as hydroxide,[10] alkoxide,[11] and acetate[12]) from outside of the coordination sphere of palladium(II) species.

$$PhN_2BF_4 + CO + NaOAc \xrightarrow[\text{1 h, room temperature}]{\text{1. Pd(OAc)}_2\text{/CH}_3\text{CN}} \xrightarrow{\text{2. PhNH}_2} \underset{83\%}{PhCOOH} + \underset{5\%}{PhCONHPh} + \underset{60\%}{CH_3CONHPh} \quad (2)$$



Application of the reaction system to the preparation of various arenecarboxylic anhydrides is in progress.

Experimental Section

Materials. All solvents were distilled and stored under nitrogen after appropriate treatment. Successive distillation from phosphorus pentoxide and calcium hydride for acetonitrile and refluxing with potassium permanganate for acetone were employed as pretreatments. Alcohols were distilled from magnesium (ethanol and *n*-butyl alcohol) or from calcium hydride (*tert*-butyl alcohol). Liquid arylamines were distilled before use under nitrogen. Guaranteed reagents of crystalline arylamines were used as received. Arenediazonium tetrafluoroborates were prepared by the ordinary method[13] and stored under nitrogen at −20 °C. 4′-Benzo-15-crown-5-diazonium hexafluorophosphate was prepared by an addition of potassium hexafluorophosphate to diazotized 4′-aminobenzo-15-crown-5, which was prepared by catalytic hydrogenation of 4′-nitrobenzo-15-crown-5.[14] Palladium acetate[15] and bis(dibenzylideneacetone)palladium[16] were prepared by published methods.

General Procedure for Carboxylation of Arenediazonium Salts. (This procedure was employed for all runs listed in Table II.) Arenediazonium tetrafluoroborate (10 mmol), sodium acetate (30 mmol), palladium acetate (0.2 mmol), and 60 mL of acetonitrile were charged to a 300-mL glass autoclave cooled to 0 °C under nitrogen. After replacement of nitrogen with carbon monoxide, 9 kg/cm^2 of carbon monoxide was introduced, and the reaction mixture was stirred for 1 h at room temperature. After a purge of carbon monoxide, acetonitrile was removed under reduced pressure, and the residue was stirred for 1 h with 20 mL of 30% aqueous sodium hydroxide. To the reaction mixture were then added 40 mL of water and 50 mL of ether. The aqueous layer was separated and the organic layer was washed once with aqueous sodium chloride. The combined aqueous layer was treated twice with active charcoal and acidified to pH 1 with concentrated

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[8] C. D. Hurd and M. F. Dull, *J. Am. Chem. Soc.*, **54**, 3428 (1932).

[9] J. M. Zeavin and A. M. Fisher, *J. Am. Chem. Soc.*, **54**, 3738 (1932).

[10] J. E. Bäckvall, B. Åkermark, and S. O. Ljunggren, *J. Am. Chem. Soc.*, **101**, 2411 (1979).

[11] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 3413 (1957).

[12] P. M. Henry and G. A. Ward, *J. Am. Chem. Soc.*, **93**, 1494 (1971); P. M. Henry, *Acc. Chem. Res.*, **6**, 16 (1973).

[13] A. Roe, *Org. React.*, **5**, 193 (1949).

[14] K. Kikukawa, K. Nagira, and T. Matsuda, *Bull. Chem. Soc. Jpn.*, **50**, 2207 (1977).

[15] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).

[16] T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organometal. Chem.*, **65**, 253 (1974).

hydrochloric acid. The aromatic carboxylic acid formed was extracted three times with ether. Removal of ether and acetic acid under reduced pressure gave the pure acid.

In the case of 4′-carboxybenzo-15-crown-5, this procedure gave crude acid contaminated with hexafluorophosphate ion. Pure 4′-carboxybenzo-15-crown-5 was obtained by washing three times with hot dilute hydrochloric acid.

Carboxylation with Bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$). A reaction mixture of diazonium salts and sodium acetate in an appropriate solvent was cooled with a dry ice–methanol bath. $Pd(dba)_2$ was added to the reaction mixture. After the introduction of 9 kg/cm^2 of carbon monoxide, the reaction mixture was warmed to room temperature and stirred for 1 h. After that, the same procedure was employed as that described above.

Carboalkoxylation of Arenediazonium Salts. Almost the same procedure as that described above was employed before workup. The reaction mixture was treated with aqueous sodium bicarbonate and extracted with ether. The aqueous layer gave benzoic acid after acidification. The organic layer was distilled under reduced pressure. The distillate was analyzed by NMR and GLC.

Registry No. Benzenediazonium tetrafluoroborate, 369-57-3; 4-methylbenzenediazonium tetrafluoroborate, 459-44-9; 3-methylbenzenediazonium tetrafluoroborate, 1422-76-0; 2-methylbenzenediazonium tetrafluoroborate, 2093-46-1; 2,6-dimethylbenzenediazonium tetrafluoroborate, 2192-33-8; 4-methoxybenzenediazonium tetrafluoroborate, 18424-07-2; 4-chlorobenzenediazonium tetrafluoroborate, 673-41-6; 3-chlorobenzenediazonium tetrafluoroborate, 14874-10-3; 2-chlorobenzenediazonium tetrafluoroborate, 1956-97-4; 4-bromobenzenediazonium tetrafluoroborate, 673-40-5; 4-iodobenzenediazonium tetrafluoroborate, 1514-50-7; 2-iodobenzenediazonium tetrafluoroborate, 7169-58-6; 4-nitrobenzenediazonium tetrafluoroborate, 456-27-9; 1-naphthalenediazonium tetrafluoroborate, 318-50-3; 4′-benzo-15-crown-5-diazonium hexafluorophosphate, 73368-13-5; methanol, 67-56-1; ethanol, 64-17-5; *tert*-butyl alcohol, 75-65-0; butanol, 71-36-3; benzoic acid, 65-85-0; 4-methylbenzoic acid, 99-94-5; 3-methylbenzoic acid, 99-04-7; 2-methylbenzoic acid, 118-90-1; 2,6-dimethylbenzoic acid, 632-46-2; 4-methoxybenzoic acid, 100-09-4; 4-chlorobenzoic acid, 74-11-3; 3-chlorobenzoic acid, 535-80-8; 2-chlorobenzoic acid, 118-91-2; 4-bromobenzoic acid, 586-76-5; 4-iodobenzoic acid, 619-58-9; 2-iodobenzoic acid, 88-67-5; 4-nitrobenzoic acid, 62-23-7; 1-naphthoic acid, 86-55-5; 4′-benzo-15-crown-5-carboxylic acid, 56683-55-7; 2,6-dimethylbenzoic anhydride, 73368-14-6; aceto-2,6-dimethylanilide, 2198-53-0; methyl 4-iodobenzoate, 619-44-3; methyl benzoate, 93-58-3; ethyl benzoate, 93-89-0; *tert*-butyl benzoate, 98-06-6; benzoic anhydride, 93-97-0; butyl benzoate, 136-60-7; benzoic 1-naphthoic anhydride, 73368-15-7; $Pd(dba)_2$, 32005-36-0; Li_2PdCl_4, 15525-45-8; $Pd(OAc)_2$, 33571-36-7.

Frontier-Controlled Pericyclic Reaction of Phencyclone with 1*H*-Azepine. Remarkably Accelerated Aromatic Cope Rearrangement of an Endo-[4 + 2]-π Cycloadduct

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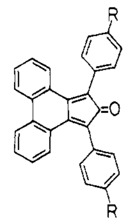
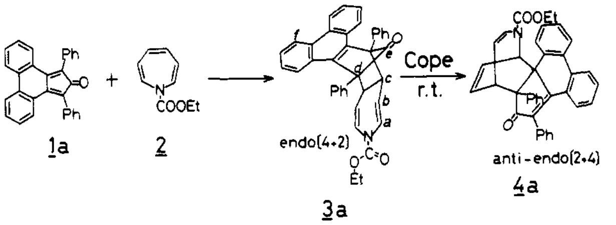
The endo-[4 + 2]-π cycloadducts of phencyclone derivatives and *N*-(ethoxycarbonyl)azepine were isolated and readily isomerized to anti-endo-[2 + 4]-π cycloadducts. The kinetics of the rearrangement of endo-[4 + 2]-π cycloadducts have been examined. The aromatic Cope rearrangement showed a first-order process with relatively low sensitivity to the ionizing power of the medium, indicating that it proceeds by a mechanism which involves very little change in charge separation between the ground state and the transition state. The rearrangement rates of endo-[4 + 2]-π cycloadducts to anti-endo-[2 + 4]-π cycloadducts were affected by changing the 2,5-substituents of the cyclopentadienones. The results can be explained in terms of the three-system interaction theory.

During the course of a study on the pericyclic reaction of phencyclone (**1a**)[1] with *N*-(ethoxycarbonyl)azepine (**2**), we have found that the endo-[4 + 2]-π cycloadduct **3a** readily undergoes aromatic Cope rearrangement to the anti-endo-[2 + 4]-π cycloadduct **4a** even at low temperature (Scheme I).



1a : R = H
1b : R = Cl
1c : R = OCH_3

Scheme I



The Cope rearrangement does not readily occur if one double bond of the 1,5-hexadiene system is incorporated in an aromatic ring. Recently, Marvell and Lin[2] demonstrated the first example of an aromatic Cope rearrangement by introducing a cyclopropane ring into the 4-

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(1) (a) Part 3 of this series. Presented in part at the 12th Congress of Heterocyclic Chemistry, Tokyo, Japan, October 24, 1979. (b) Part 2: Yasuda, M.; Harano, K.; Kanematsu, K., *J. Org. Chem.* 1980, *45*, 659–64.

(2) Marvell, E. N.; Lin, C., *J. Am. Chem. Soc.* 1978, *100*, 877–83, and references cited therein.

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