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Reductive Formylation of Aromatic Halides under Low Carbon Monoxide Pressure Catalyzed by Transition-Metal Compounds

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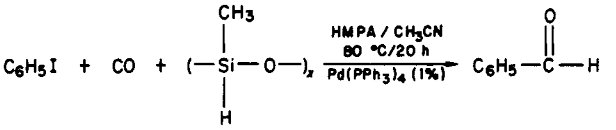
Substituted aryl halides were formylated under 50 psi pressure of carbon monoxide in the presence of a hydrogen donor such as poly(methylhydrosiloxane) (PMHS) and a homogeneous transition-metal catalyst to give aromatic aldehydes in good yields. Addition of an amine was necessary to trap the hydrogen halide formed. Sodium formate could serve as a hydrogen donor in the absence of a base. Conditions for selective formylation of one position in dihalobenzenes such as iodobromobenzenes and bromochlorobenzenes were developed. Various transition-metal catalysts were examined, of which palladium compounds were found to be most efficient.

Introduction

The carbonylation of organic halides in the presence of palladium catalysts is well-known and has been reported in recent publications concerning the synthesis of esters,[1] amides,[2] ketones,[3] and carboxylic acids derivatives.[4] Aldehydes are prepared in a similar reaction under high pressure of carbon monoxide and hydrogen.[5] The usefulness of the last reaction is limited by the need to manipulate pressurized hydrogen and carbon monoxide (1500 psi) in a high-pressure reaction apparatus. We wish to report here a convenient low-pressure formylation reaction which may be used to prepare aldehydes from aryl and benzyl halides.

Results and Discussion

When iodobenzene was reacted under 50 psi of carbon monoxide gas, in the presence of poly(methylhydrosiloxane) (PMHS) as a hydrogen donor and acetonitrile as a solvent, 68% of benzaldehyde was isolated (96% GC yield) after 20 h of reaction at 80 °C (Table I, entry 1). Hexamethylphosphoramide (HMPA) served as a cosolvent and as a base and tetrakis(triphenylphosphine)palladium(0) (1%) as the catalyst (eq 1). PMHS which we used as


(1)

$$C_6H_5I + CO + (-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{Si}}-O-)_x \xrightarrow[Pd(PPh_3)_4\ (1\%)]{HMPA\ /\ CH_3CN,\ 80\ ^\circ C/20\ h} C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-H \quad (1)$$

a hydrogen donor is a mild, air stable, reducing agent[6] and has the advantages of having a high flash point (120 °C) and being relatively inexpensive.

As bromobenzenes proved not to react under these conditions it is possible to selectively formylate bromoiodoarenes at one position. Thus, 4-iodobromobenzene was converted in 95% yield into 4-bromobenzaldehyde (Table I, entry 2).

In order to affect also bromobenzene derivatives, somewhat more drastic conditions had to be applied; the reaction of bromobenzene in a solution of acetonitrile: dimethyl sulfoxide (Me_2SO) (1:1) containing 3% tetrakis(triphenylphosphine)palladium(0) and tribenzylamine as a base yielded 59% of benzaldehyde (Table I, entry 3). The reaction was found to be highly chemoselective and the only detected side product was benzophenone (0.5%). A quantity of 35% of the starting bromobenzene remained unreacted, whereas under the same experimental conditions, iodobenzene reacted to give 96% of benzaldehyde (Table I, entry 19). Chlorobenzene did not react, even under these conditions, and the formylation of 4-bromochlorobenzene resulted in the formation of 4-chlorobenzaldehyde as the only product (54% yield) (Table I, entries 4 and 23). Reductive carbonylation was performed on a number of substituted aromatic halides (Table I, entries 5–13) and was shown to be highly dependent on electronic and steric changes in the substrate. The carbonylation reaction was also applied to benzyl bromide which, under the same conditions, gave 36% yield of the isolated phenylacetaldehyde (Table I, entry 10). Attempts to carbonylate α-bromo ketones (e.g., α-bromoacetophenone) resulted in the quantitative reductive debromination of the starting materials.

Various palladium compounds were found to act as catalysts in the reductive carbonylation of aryl halides. The Pd(0) complex tetrakis(triphenylphosphine)palladium(0) and the Pd(II) complex palladium(II) diacetate were found to catalyze the reaction to a similar extent (Table I, entries 1 and 14). Bis(triphenylphosphine)palladium(II) dichloride, supported on polystyrene (cross-linked with 2% divinylbenzene) catalyzed the reaction[7] with excellent yields for two successive runs (Table I, entries 16 and 17), even after prolonged exposure of the catalyst to air between the first and second runs. A lower catalytic activity was found for benzylbis(triphenylphosphine)palladium(II) chloride and for tricarbonyl(triphenylphosphine)cobalt dimer (Table I, entries 15 and 18). Hydridocarbonyltris(triphenylphosphine)rhodium did not catalyze the reaction at all. Attempts to use various alkyl amines as scavengers for the formed hydrogen halide caused rapid precipitation

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(1) (a) Martin, L. D.; Stille, J. K. *J. Org. Chem.* **1982**, *47*, 3630. (b) Tanaka, M.; Koyanagi, M.; Kobayashi, T. *Tetrahedron Lett.* **1981**, *22*, 3875. (c) Murray, T. F.; Samsel, E. G.; Varma, V.; Norton, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 7520. (d) Cowell, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4193.

(2) (a) Ozawa, F.; Soyama, H.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* **1982**, *23*, 3383. (b) Ishikura, M.; Mori, M.; Terashima, M.; Ban, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 741. (c) Kobayeshi, T.; Tanaka, M. *J. Organomet. Chem.* **1982**, *233*, C-64.

(3) (a) Koshiaki, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1981**, 333. (b) Kikukowa, K.; Kono, K.; Wada, F.; Matsuda, T. *Chem. Lett.* **1982**, 35. (c) Tanaka, M. *Tetrahedron Lett.* **1979**, *20*, 2601.

(4) (a) Kikukawa, K.; Kono, K.; Wada, F.; Matsuda, T. *Tetrahedron Lett.* **1980**, *21*, 2877. (b) Nagira, K.; Kikukawa, K.; Wada, F.; Matsuda, T. *J. Org. Chem.* **1980**, *45*, 2365. (c) Tanaka, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 637.

(5) (a) Yoshida, H.; Sugita, N.; Kudo, K.; Takezaki, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1681. (b) Schoenberg, A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 7761.

(6) Lipowitz, J.; Bowman, S. A. *J. Org. Chem.* **1973**, *38*, 162.

(7) The efficiency of polymer-bonded catalysts in hydrogen-transfer reactions was demonstrated: Azran, J.; Buchman, O.; Orchin, M.; Blum, J. *J. Org. Chem.* **1984**, *49*, 1327.

0022-3263/84/1949-4009$01.50/0

Table I. Formylation of Aromatic Halides with PMHS as a Hydrogen Donor[a]

entry	halide (mmol)	catalyst (mmol)	base (mmol)	PMHS, mL	reactn temp, °C	product,[b] (% yield)
1	C_6H_5I (5.0)	$Pd(PPh_3)_4$ (0.05)	HMPA (15)	2.0	80[c]	C_6H_5CHO (96) (68)[d]
2	4-BrC_6H_4I (1.0)	$Pd(PPh_3)_4$ (0.01)	HMPA (3)	0.4	80[c]	4-BrC_6H_4CHO (95)
3	C_6H_5Br (1.0)	$Pd(PPh_3)_4$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	C_6H_5CHO (59)
4	4-ClC_6H_4Br (1.0)	$Pd(PPh_3)_4$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	4-ClC_6H_4CHO (54)
5	2-$CH_3C_6H_4I$ (1.0)	$Pd(PPh_3)_4$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	2-$CH_3C_6H_4CHO$ (23)
6	2-$CH_3C_6H_4Br$ (1.0)	$Pd(PPh_3)_4$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	2-$CH_3C_6H_4CHO$ (2)
7	4-$CH_3C_6H_4Br$ (1.0)	$Pd(PPh_3)_4$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	4-$CH_3C_6H_4CHO$ (48)
8	2-$CH_3OC_6H_4Br$ (1.0)	$Pd(PPh_3)_4$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	2-$CH_3OC_6H_4CHO$ (14)
9	4-$CH_3OC_6H_4Br$ (1.0)	$Pd(PPh_3)_4$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	4-$CH_3OC_6H_4CHO$ (35)
10	$C_6H_5CH_2Br$ (5.0)	$Pd(PPh_3)_4$ (0.15)	$(C_6H_5CH_2)_3N$ (7.0)	2.0	110	$C_6H_5CH_2CHO$ (36)[d]
11	1-bromonaphthalene (1.0)	$Pd(PPh_3)_4$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	125	1-naphthaldehyde (61)
12	2-bromothiophene (1.0)	$Pd(PPh_3)_4$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	125	2-thiophenecarboxaldehyde (82)
13	4-NCC_6H_4Br (1.0)	$Pd(PPh_3)_4$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	125	4-NCC_6H_4CHO (48)
14	C_6H_5I (1.0)	$Pd(OAc)_2$ (0.1)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	C_6H_5CHO (95)
15	C_6H_5Br (1.0)	$PhCH_2PdCl(PPh_3)_2$	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	C_6H_5CHO (69)
16	C_6H_5I (1.0)	$PdCl_2(PPh_3)_2$, 3% on polymer (first run)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	C_6H_5CHO (85)
17	C_6H_5I (1.0)	$PdCl_2(PPh_3)_2$, 3% on polymer (2nd run)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	C_6H_5CHO (94)
18	C_6H_5I (1.0)	$(Co(CO)_3PPh_3)_2$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	C_6H_5CHO (18)
19	C_6H_5I (1.0)	$Pd(PPh_3)_4$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	C_6H_5CHO (96)
20	C_6H_5I (1.0)	$Pd(PPh_3)_4$ (0.03)	pyridine (2.0)	0.4	110	C_6H_5CHO (16)
21	C_6H_5I (1.0)	$Pd(PPh_3)_4$ (0.03)	$H_3CN(Oct)_2$ (2.0)	0.4	110	*e*
22	C_6H_5I (1.0)	$Pd(PPh_3)_4$ (0.03)	$Ca(OH)_2$ (2.0)	0.4	110	*e*
23	C_6H_5Cl (1.0)	$Pd(PPh_3)_4$ (0.03)	$(C_6H_5CH_2)_3N$ (1.4)	0.4	110	*e*

[a] CO initial pressure 50 psi; reaction time 18 h. [b] Yields determined by GC or HPLC unless otherwise stated. [c] Reaction time 20 h. [d] Isolated yield. [e] No reaction.

Table II. Formylation of Aryl Halides with Sodium Formate as the Hydrogen Donor[a]

entry	halide (mmol)	catalyst (mmol)	sodium formate (mmol)	product[b] (% yield)
1	C_6H_5I (1.0)	$Pd(PPh_3)_4$ (0.03)	6.0	C_6H_5CHO (72)
2	C_6H_5I (1.0)	$Pd(PPh_3)_4$ (0.04)	10.0	C_6H_5CHO (80)
3	C_6H_5Br (1.0)	$Pd(PPh_3)_4$ (0.03)	6.0	C_6H_5CHO (45)
4	C_6H_5Br (1.0)	$Pd(PPh_3)_4$ (0.04)	10.0	C_6H_5CHO (58)
5	C_6H_5Cl (1.0)	$Pd(PPh_3)_4$ (0.05)	6.0	*c*

[a] Carbon monoxide initial pressure 50 psi at room temperature; reaction temperature 125 °C; reaction time 18 h. [b] Yields determined by HPLC. [c] No reaction.

of metalic palladium and consequently no carbonylation occurred (Table I, entry 21). Pyridine gave somewhat better yields and no catalyst precipitation took place (Table I, entry 20). However, the use of tribenzylamine resulted in high yields of the desired aldehyde. Inorganic bases (e.g., $Ca(OH)_2$ which has been reported[8] to act as HBr scavanger in nickel-catalyzed conversion of bromobenzene to benzoic acid) did not react under our conditions (Table I, entry 22). PMHS could be successfully substituted by sodium formate as a hydrogen donor. Good yields of aldehyde were obtained using a 6–10-fold excess of sodium formate (Table II). The formylation of aryl halide with carbon monoxide and sodium formate could be accomplished in the absence of a base. An equimolar amount of CO_2 is formed in this process (eq 2), as proven by GC

$$C_6H_5X + CO + HCO_2Na \xrightarrow[Pd(PPh_3)_4\ (3\%)]{CH_3CN/Me_2SO\ 120\ °C/18\ h} C_6H_5CHO + CO_2 + NaX \quad (2)$$

analysis of the gas phase once the reaction was terminated. The scope of the last reaction is now under investigation.

The mechanism of formylation with PMHS/CO seems to have common features with the mechanism of high-pressure H_2/CO formylations.[9] Such a mechanism, which was suggested by Heck,[5b] involves a reduction of acylpalladium intermediate. In fact, benzoyl chloride was found to be hydrogenated by PMHS in acetonitrile solution containing tetrakis(triphenylphosphine)palladium(0) and tribenzylamine to give benzaldehyde. The detailed transformations of the PMHS in the reaction are still obscure: cleavage of the Si–H bond throughout the reaction could be observed by vanishing of its ^1H NMR signal at 4.71 ppm followed by the appearance of the benzaldehyde signal at 10.00 ppm. (The liberation of molecular hydrogen from PMHS under the reaction conditions was found by GC to be ≤1%.) A plausible mechanism for PMHS activation is the formation of a hydridopalladiumsiloxane complex analogous to the recently reported iridium and rhodium complexes,[10] which were found to result from direct reaction of hydrosiloxanes and transition metal complexes. The reaction of such an hydrido complex with aryl halide followed by HX elimination, carbonylation, and a second Si–H abstraction may then take place.

Experimental Section

General Procedures. ^1H NMR spectra were obtained on a Varian EM 360 instrument. HPLC separations were performed on a Varian 5000 with a MCH-5 column (4.0 mm × 15 cm) and 35% H_2O in MeCN as eluent. GC determinations of CO_2 were performed on HP Gas Chromatograph Model 7620A using ($^1/_4$ in. × 6 ft) 13X molecular sieve and Porapak R columns. Reactions were performed in glass pressure reaction vessels provided with

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[8] Cassar, L.; Foa, M. *J. Organomet. Chem.* **1973**, *51*, 381.

[9] A related similarity in reactivities of molecular hydrogen and organohydrosilane toward transition metal complexes is discussed: Nurai, S.; Sonuda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837.

[10] Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

a magnetic stirrer and connected to a pressure gauge.

Formylation of Iodobenzene with PMHS in MeCN/HMPA. Tetrakis(triphenylphosphine)palladium(0) (50 mg, 0.05 mmol) was placed in the reaction vessel which was then purged with nitrogen. Acetonitrile (20 mL), HMPA (2.5 mL), PMHS (2.0 mL), and iodobenzene (0.5 mL, 4.5 mmol) were introduced via a syringe through a rubber septum into the vessel. The reaction vessel was purged twice with carbon monoxide and then loaded with 50 psi of carbon monoxide at room temperature. The mixture was stirred at 80 °C for 20 h. After 20 h the reaction mixture was cooled to room temperature, ether (100 mL) was added, the mixture was filtered from solid polymer residue, and the volatile solvents were removed (rotoevaporator). The resulting yellow oil was dissolved in 30 mL of ether, washed with three portions of 30 mL of water, and dried with $MgSO_4$ and the ether was removed under reduced pressure. *n*-Hexane (50 mL) was added and the formed precipitate was removed by filtration followed by evaporation of the *n*-hexane. Benzaldehyde (310 mg, 3 mmol) was isolated by Kugelrohr distillation. The pot residue consists of an oily material which had only one ^1H NMR signal at 0.15 ppm (Si–CH_3).

Formylation of Bromobenzene in MeCN/Me_2SO Solution. A mixture of 150 mg (0.15 mmol) of $Pd(PPh_3)_4$ and 2.65 g of tribenzylamine (9.2 mmol) was placed in the reaction vessel. After the mixture was purged with nitrogen, acetonitrile (10 mL), Me_2SO (10 mL), PMHS (20 mL), and bromobenzene (0.5 mL, 4.8 mmol) were introduced via a syringe through a rubber septum. Carbon monoxide (50 psi) was added at room temperature and the sealed reaction vessel was heated to 110 °C for 18 h. After workup as described before, 300 mg (2.8 mmol) of benzaldehyde were separated by Kugelrohr distillation.

Formylation of Bromobenzene with Sodium Formate as the Hydrogen Donor. A mixture of 50 mg (0.05 mmol) of $Pd(PPh_3)_4$ and 400 mg (6 mmol) of sodium formate was placed in the reaction vessel. After the mixture was purged with nitrogen, acetonitrile (4 mL), dimethyl sulfoxide (4 mL), and bromobenzene (0.1 mL, 0.95 mmol) were added via a syringe through a rubber septum. Carbon monoxide (50 psi) was introduced at room temperature and the sealed reaction vessel was heated to 125 °C. After 18 h the reaction mixture was cooled to room temperature, methanol (30 mL) was added, and benzaldehyde (63.7 mg, 0.60 mmol) was determined by HPLC in the crude filtered methanol solution.

Registry No. HMPA, 680-31-9; PMHS, 9004-73-3; C_6H_5I, 591-50-4; 4-BrC_6H_4I, 589-87-7; C_6H_5Br, 108-86-1; 4-ClC_6H_4Br, 106-39-8; 2-$CH_3C_6H_4I$, 615-37-2; 2-$CH_3C_6H_4Br$, 95-46-5; 4-$CH_3C_6H_4Br$, 106-38-7; 2-$CH_3OC_6H_4Br$, 578-57-4; 4-$CH_3OC_6H_4Br$, 104-92-7; $C_6H_5CH_2Br$, 100-39-0; 4-NCC_6H_4Br, 623-00-7; C_6H_5Cl, 108-90-7; C_6H_5CHO, 100-52-7; 4-BrC_6H_4CHO, 1122-91-4; 4-ClC_6H_4CHO, 104-88-1; 2-$CH_3C_6H_4CHO$, 529-20-4; 4-$CH_3C_6H_4CHO$, 104-87-0; 2-$CH_3OC_6H_4CHO$, 135-02-4; 4-$CH_3OC_6H_4CHO$, 123-11-5; $C_6H_5CH_2CHO$, 122-78-1; 4-NCC_6H_4CHO, 105-07-7; $Pd(PPh_3)_4$, 14221-01-3; $Pd(OAc)_2$, 3375-31-3; $PhCH_2PdCl(PPh_3)_2$, 22784-59-4; $PdCl_2(PPh_3)_2$, 13965-03-2; $(Co(CO)_3PPh_3)_2$, 10170-27-1; $(C_6H_5CH_2)_3N$, 620-40-6; $Ca(OH)_2$, 1305-62-0; CO, 630-08-0; $H_3CN(Oct)_2$, 4455-26-9; 1-bromonaphthalene, 90-11-9; 2-bromothiophene, 1003-09-4; 1-naphthaldehyde, 66-77-3; 2-thiophenecarboxaldehyde, 98-03-3; pyridine, 110-86-1; sodium formate, 141-53-7.

Oxidative Deamination of Amines by Arylsulfonyl Peroxides[1]

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Oxidation of primary and secondary amines with arylsulfonyl peroxides **1a**,**b** was examined. Optimal results were obtained by using *m*-(trifluoromethyl)benzenesulfonyl peroxide, **1b**, as the oxidant and potassium hydroxide as the promoting base in ethyl acetate at −78 °C. Under these conditions, yields of carbonyl products were generally higher than other methods for both amine types. The stability of the intermediate imine is of great importance in determining the success of the conversion.

It was previously reported that amines could be oxidatively deaminated to carbonyl products with arylsulfonyl peroxides.[2] This synthetic transformation, oxidative deamination,[3] has been the subject of numerous studies using a variety of oxidizing agents,[4] peroxides,[5] and synthetic sequences.[6-12] These methods are subject to limitations of amine type and/or problems of overoxidation. Probably the best procedure for primary amines is the biomimetic method of Rapoport,[10] while for secondary amines, the most successful method is the superoxide-

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[1] (a) Taken in part from the Ph.D. Thesis of A.K. submitted to the Graduate School of New Mexico State University, October, 1983. (b) Part 8 in the "The Oxidation of Amines with Sulfonyl Peroxide". For part 7, see: Hoffman, R. V.; Belfoure, E. L. *Synthesis* **1983**, 34.

[2] Hoffman, R. V. *J. Am. Chem. Soc.* **1976**, *98*, 6702.

[3] Baumgarten, R. J. *J. Chem. Educ.* **1966**, *43*, 398.

[4] (a) $Pb(OAc)_4$: Sisti, A. J.; Milstein, S. R. *J. Org. Chem.* **1974**, *39*, 3932. Stojiljkovic, A.; Andrejcvic, V.; Mehailovic, M. L. *Tetrahedron* **1967**, *23*, 721. (b) MnO_2: Pratt, E. F.; McGovern, T. P. *J. Org. Chem.* **1964**, *29*, 1540. (c) $KMnO_4$: Shechter, H.; Rawalay, S. S.; Tubio, M. *J. Am. Chem. Soc.* **1964**, *86*, 1701. Shechter, H.; Rawalay, S. S. *Ibid.* **1964**, *86*, 1706. Rawalay, S. S.; Shechter, H. *J. Org. Chem.* **1967**, *32*, 3129. (d) NiO_2: George, M. V.; Balachandran, K. S. *Chem. Rev.* **1975**, *75*, 491. (e) Ag_2CO_3: Fetizon, M.; Golfier, M.; Milcent, R.; Papadakis, L. *Tetrahedron* **1975**, *31*, 165. (f) Cu(I), O_2: Kametani, T.; Takahashi, K.; Ohsawa, T.; Ihara, M. *Synthesis* **1977**, 245. (g) $(CuX_2NO)_2$: Doyle, M. P.; Siegfried, B.; Hanmond, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 1628. (h) NaOCl: Lee, G. A.; Freedman, H. H. *Tetrahedron Lett.* **1976**, 1641. (i) Sulfuranes: Franz, J. A.; Martin, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 583. (j) Selenuranes: Marino, J. P.; Larsen, R. O., Jr. *Ibid.* **1981**, *103*, 4642.

[5] (a) $Na_2S_2O_8$–$AgNO_3$: Bacon, R. G. R.; Stewart, D. *J. Chem. Soc. C* **1968**, 1384. (b) Hydroperoxides: De La Mare, H. E. *J. Org. Chem.* **1960**, *25*, 2114. (c) Acyl peroxides: Huisgen, R.; Bayerlein, F. *Liebigs Ann. Chem.* **1960**, *630*, 138.

[6] Eliminations in *N*-chloramines promoted by: (a) Na_2CO_3: Ruenitz, P. C.; Smissman, E. E. *J. Org. Chem.* **1977**, *42*, 937. (b) Alkoxides: Bachmann, W. E.; Cava, M. P.; Dreiding, A. S. *J. Am. Chem. Soc.* **1954**, *76*, 5554. Guillemin, J. C.; Denis, J. M.; Lablanche-Combier, A. *Ibid.* **1981**, *103*, 468. (c) KO_2: Scully, F. E., Jr. *J. Org. Chem.* **1980**, *45*, 1515. Scully, F. E., Jr.; Davis, R. C. *Ibid.* **1978**, *43*, 1467. Meyers, A. E.; Himmelsbach, R. J.; Reuman, M. *Ibid.* **1983**, *48*, 4053. Scully, F. E., Jr.; Schlager, J. J. *Heterocycles* **1982**, *19*, 653.

[7] Conversion to selenenic amides followed by elimination: Czarny, M. R. *Synth. Commun.* **1976**, *6*, 285; *J. Chem. Soc., Chem. Commun.* **1976**, 81.

[8] Conversion to sulfinamides followed by elimination: Trost, B. M.; Liu, G. *J. Org. Chem.* **1981**, *46*, 4617.

[9] Oxidation of Schiff bases: Dinizo, S. E.; Watt, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 6900.

[10] Biomimetic approaches involving the isomerization of Schiff bases: Babler, J. H.; Invergo, B. J. *J. Org. Chem.* **1981**, *46*, 1937. Buckley, T. F.; Rapoport, H. *J. Am. Chem. Soc.* **1982**, *104*, 4446.

[11] Oxidation to the nitro compound with ozone followed by elimination: Keinan, E.; Mazur, Y. *J. Am. Chem. Soc.* **1978**, *99*, 3861; *J. Org. Chem.* **1977**, *42*, 844.

[12] Electrochemical oxidation of amine derivatives: Shono, T.; Matsumura, Y.; Kashimura, S. *J. Org. Chem.* **1983**, *48*, 3338. Semmelhack, M. F.; Schmid, C. R. *J. Am. Chem. Soc.* **1983**, *105*, 6732.

0022-3263/84/1949-4011$01.50/0