of ZnTPP. Workup gave 323 mg (0.476 mmol, 92%) of ZnTPP, 3.7 mg (0.005 mmol, 1%) of **5**, and 4 mg (0.006 mmol, 1%) of **7**.

Reaction of $ZnTPP^{+}\cdot,ClO_4^-$ with Solid Sodium Nitrite in Methylene Chloride. A solution of 445 mg of $ZnTPP^{+}\cdot,ClO_4^-$ (95% pure, 0.544 mmol) in 30 mL of methylene chloride was stirred for 48 h with 291 mg (4.22 mmol) of solid sodium nitrite. The visible spectrum had λ_{max} 846, 765, 586, 549, 510, 421, and 400 nm, indicating the presence of ZnTPP and either **7** or an isoporphyrin. Workup gave 6 mg (0.0098 mmol, 1.8%) of TPP, 176 mg (0.26 mmol, 48%) of ZnTPP, 126 mg (0.174 mmol, 32%) of **5**, and 66 mg (0.102 mmol, 19%) of **7**.

Reaction of $ZnTPP^{+}\cdot,ClO_4^-$ with Solid Sodium Nitrite and Urea in Methylene Chloride. A reaction similar to that above was carried out with 550 mg of $ZnTPP^{+}\cdot,ClO_4^-$ (91% pure, 0.645 mmol), 247 mg (3.58 mmol) of sodium nitrite, and 2.14 g (35.7 mmol) of urea. The solution slowly turned grey-brown. After 40 h the visible spectrum showed weak bands characteristic of either **7** or an isoporphyrin. Workup gave 4.2 mg (0.0068 mmol, 1%) of TPP, 215 mg (0.318 mmol, 49%) of ZnTPP, 130 mg (0.180 mmol, 28%) of **5**, and 63 mg (1.01 mmol, 15%) of **7**.

Identification of $ZnTPP-NO_2$ (5) and the Bilitriene (7). Products from the reactions of sodium nitrite and water with $ZnTPP^{+}\cdot$ (i.e., TPP and ZnTPP) were identified by their visible and mass spectra and occasionally by TLC. $ZnTPP-NO_2$, mp >360 °C, was identified by mass spectrum (*m/e* found 721.147 55, calcd 721.1356), ^1H NMR, and elemental analysis.

Anal. Calcd for $C_{44}H_{27}ZnN_5O_2$ (**5**): C, 73.1; H, 3.76; N, 9.68. Found: C, 73.2; H, 3.90; N, 9.52.

^1H NMR [$(CD_3)_2C{=}O$] δ 9.10 (s, 1 H, β-H), 8.84 (s, 6 H, β-H), 8.30–8.10 (m, 8 H, *o*-H), 7.90–7.60 (m, 12 H, *m*- and *p*-H).

The bilitriene (**7**), mp 140–144 °C, was identified by mass spectrometry and by comparison of its ^1H NMR absorption spectra with those of a sample supplied by Professor K. M. Smith.[39] The spectra were identical in all aspects except for weak NMR signals attributable to small amounts of impurity.

Reaction of $ZnTPP^{+}\cdot,ClO_4^-$ with Methanol. Formation of $ZnTPP-OMe^{+},ClO_4^-$ (10). To 35 mL of methanol which had been distilled from magnesium and iodine was added 787 mg of $ZnTPP^{+}\cdot,ClO_4^-$ containing 0.86 mmol (85%) of $ZnTPP^{+}\cdot$. After being stirred overnight, the red solution was concentrated and chromatographed on a column of silica. Elution with chloroform gave a mixture of TPP and ZnTPP which was separated later on a column of alumina (activity I) into 36 mg of TPP and 233 mg of ZnTPP. Elution with ether gave 57 mg of solids which were discarded. Elution with acetone gave 427 mg of brown solid, part of which was rechromatographed on silica to give 307 mg (0.379 mmol, 44%) of **10**. Three crystallizations of part of the brown solid from benzene–petroleum ether gave brown granular crystals which did not melt below 360 °C.

Anal. Calcd for $C_{45}H_{31}ZnN_4ClO_5$ (**10**): C, 66.8; H, 3.87; N, 6.93; Cl, 4.38. Found: C, 66.6, 66.7; H, 4.43, 4.16; N, 6.74; Cl, 4.03.

^1H NMR [C_6D_6] δ 7.06 (m, 20 H, phenyl protons), 6.56 (m, 6 H, β-H), 6.28 (d, 2 H, J = 4.5 Hz, β-H), 3.58 (br s, 3 H, Me).

Reaction of $ZnTPP^{+}\cdot,ClO_4^-$ with Ammonia and Amines. Formation of ZnTPP. In separate experiments, ammonia, methylamine, and dimethylamine were bubbled into solutions of $ZnTPP^{+}\cdot,ClO_4^-$ in acetonitrile. In each case the solution turned red. Workup and chromatography on alumina (activity III) gave ZnTPP in yields of 91% (ammonia), 100% (methylamine), and 86% (dimethylamine). Some small bands were also seen on the columns but were not collected.

Absorption Spectra. These were recorded with solutions in methylene chloride and are given in λ nm ($10^{-4}\epsilon$): **1**, 594 (1.28), 555 (1.67), 520 sh (0.572), 427 (27.0); **2**, 601 (1.61), 561 (1.43), 527 sh (0.484), 433 (36.9); **3**, 597 (1.59), 558 (1.74), 524 sh (0.483), 490 sh (0.212), 431 (43.1); **4**, 586 (0.567), 551 (2.45), 515 (0.383), 485 sh (0.183), 426 (48.4); **5**, 597 (1.02), 555 (1.55), 520 sh (0.391), 426 (21.7); **6**, 656 (1.16), 601 (0.514), 560 sh (0.413), 525 (1.71), 425 (24.9).[40]

Registry No. **1**, 60165-30-2; **1**-d_5, 71435-51-3; **2**, 71435-53-5; **3**, 71435-55-7; **4**, 71435-56-8; **5**, 71435-57-9; **6**, 60148-22-3; **7**, 63160-30-5; **10**, 25895-68-5; TPP, 917-23-7; ZnTPP, 14074-80-7; $ZnTPP^{+}\cdot ClO_4^-$, 34465-02-6; pyridine, 110-86-1; pyridine-d_5, 7291-22-7; triphenylphosphine, 603-35-0; triphenylarsine, 603-32-7; sodium thiocyanate, 540-72-7; sodium nitrite, 7632-00-0; potassium nitrite, 7758-09-0; methanol, 67-56-1; ammonia, 7664-41-7; methylamine, 74-89-5; dimethylamine, 124-40-3.

(39) We thank Professor Smith for sending us copies of his spectra and a sample of his bilitriene and for comparing also in his laboratory a sample of our bilitriene with that isolated in Liverpool.

(40) We thank Dr. Kiyoshi Iwai for assistance in recording these data.

Chromium(VI) Oxidations of Alkynes

W. B. Sheats, L. K. Olli, R. Stout, J. T. Lundeen, R. Justus, and W. G. Nigh*

Department of Chemistry, University of Puget Sound, Tacoma, Washington 98416

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The distribution of products from the reaction of several chromium(XI) reagents with various alkynes was studied in order to determine the most efficient reagent for α-oxidation. Chromic acid, chromyl acetate, chromyl chloride, *tert*-butyl chromate, chromium trioxide–pyridine complex, and pyridinium chlorochromate were compared with regard to their ability to oxidize diphenylethyne, 1-phenyl-1-ethyne, 1-phenyl-1-ethyne, 2-decyne, 5-decyne, 4-octyne, and 7-tetradecyne. The chromium trioxide–pyridine complex and pyridinium chlorochromate were found to be the most efficient reagents for preparing conjugated ynones.

Chromium(VI) and manganese(VII) are two of the strongest and most commonly used oxidizing agents for organic compounds. These reagents, however, exhibit quite different selectivities. Chromium(VI) oxidizing agents have been used extensively in organic synthesis[1a-e] and in particular are useful for the conversion of primary alcohols to aldehydes[2a-g] and carboxylic acids and secondary alcohols to ketones. In addition, chromium(VI) reagents have been used to prepare α,β-unsaturated carbonyl compounds. While manganese(VII) rapidly reacts directly with the π

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Table I. Chromic Acid Oxidation of Alkynes

alkyne	% of H_2SO_4	T, °C	reaction time, min	% of unreacted $RC{\equiv}CCH_2R'$	% of $RC(O)C(O)CH_2R'$	% of RCO_2H	% of $RC{\equiv}CC(O)R'$
diphenylethyne	0	23	10	100	0	0	
	2	23	10	<1	27	73	
	4	23	10	<1	30	70	
	6	23	10	<1	35	65	
	10	23	10	3	96	1	
1-phenyl-1-propyne	0	27	1080	~100	trace	trace	trace
	0	118	1830	31	6	61	2
	2	23	10	17	24	58	1
	4	23	10	1	16	82	1
	6	23	10	<1	8	90	2
	8	23	10	2	24	73	2
	10	23	10	3	32	64	2
1-phenyl-1-butyne	0	23	10	100	0	0	0
	2	23	10	21	19	60	0
	4	23	10	5	32	63	0
	6	23	10	4	36	60	0
	8	23	10	2	34	64	0
	10	23	10	7	34	59	0

bond of alkenes and alkynes[3a,b] to yield 1,2-diols, 1,2-diketones, and carboxylic acids, chromium(VI) reagents oxidize alkenes and alkynes slowly and often immediately adjacent to the π bond.

$$RCH{=}CHR \xrightarrow{MnO_4^-} RC(OH)HC(OH)HR \xrightarrow{MnO_4^-} RC(O)C(O)R \xrightarrow{MnO_4^-} 2RCO_2H$$

$$RC{\equiv}CR \xrightarrow{MnO_4^-} RC(O)C(O)R + RCO_2H$$

$$RCH{=}CHCH_2R' \xrightarrow{Cr(VI)} RC(O)C(O)CH_2R' + RCO_2H + R'CH_2CO_2H + RCH{=}CHC(O)R'$$

$$RC{\equiv}CCH_2R' \xrightarrow{Cr(VI)} RC(O)C(O)CH_2R' + RCO_2H + R'CH_2CO_2H + RC{\equiv}CC(O)R'$$

These α-oxidations have been effected with chromyl acetate,[4] chromic acid,[5] *tert*-butyl chromate,[6] and the chromium trioxide–pyridine complex.[7] However, there are several chromium(VI) species which have not been studied with respect to their ability to allylically oxidize alkenes. In addition, there has been only one report of chromium(VI) α-oxidation of alkynes.[8]

We have attempted to determine the scope and effectiveness of the α-oxidation of alkynes, using a variety of chromium(VI) reagents and diphenylethyne, 1-phenyl-1-propyne, and 1-phenyl-1-butyne. In some of the later experiments, several aliphatic alkynes were also studied. The reaction products were analyzed by gas–liquid chromatography (GC) and the readily isolated products characterized by their melting points and their infrared and proton magnetic resonance spectra. The reaction products which were difficult to isolate and purify were characterized by gas chromatographic/mass spectral (GC/MS) analysis or by derivatization (2,4-dinitrophenylhydrazones) and thin-layer chromatography. The results of these experiments are presented in Tables I and II.

As the data in Table I indicate, the chromic acid oxidation is strongly acid catalyzed and tends to give nearly exclusive oxidation of the triple bond. On the other hand, chromyl chloride, chromyl acetate, and *tert*-butyl chromate were found to give a mixture of direct and α-oxidation products (cf. Table II). The reagent produced by the reaction of chromium trioxide and *tert*-butyl alcohol has generally been described as di-*tert*-butyl chromate, but recent evidence presented by Sharpless and Akashi[2e] suggests that at least a portion of the reagent is the half-acid ester. Although it has been reported that di-*tert*-butyl chromate is superior to the chromium trioxide–pyridine complex for allylic oxidation,[2e] the reverse seems to be true for the α-oxidation of alkynes. Only the chromium trioxide–pyridine complex (Sarett reagent) and pyridinium chlorochromate gave nearly exclusive α-oxidation of alkynes. Of these two oxidizing agents, the Sarett reagent gives more rapid formation of products and thus appears to be still the reagent of choice for α-oxidations. Longer reaction times and somewhat higher reaction temperatures would be expected to improve the yields without the danger of increasing the amount of side products. Regardless of which of these reagents is used, the reaction yields large amounts of black tar which is difficult to remove from the desired products, and it is highly recommended that a combination of Sharpless's[2e] and Corey's[2f] workup procedures be used. The chromium trioxide on the graphite reagent[2g] was completely unreactive toward alkynes.

Experimental Section

The alkynes used in this work were purchased from the Farchan Division of the Story Chemical Corp. All of these chemicals were found to be chromatographically pure and were used directly without further purification. Authentic samples of expected reaction products were either obtained from commercial sources or synthesized by standard laboratory procedures. The chromatographic analyses were carried out with a Pye M-104 equipped with a flame ionization detector, using 5 ft × $^1/_8$ in. (i.d.) glass and 9 ft × $^1/_8$ in. (o.d.) stainless steel columns packed with 1.5% OV-225 on 100–120 mesh Chromosorb G-HP. Infrared spectra were recorded on a Beckman IR-12 spectrometer, and the proton magnetic resonance spectra were obtained on a Varian T-60 spectrometer. The GC/MS analyses were carried out on a Finnigan M-3000 interfaced to a Varian M-1400 gas chromatograph.

Chromic Acid in Acetic Acid. Sodium dichromate dihydrate (1.5 g, 0.005 mol) was dissolved in glacial acetic acid (25 mL) and the appropriate amount of concentrated sulfuric acid added. The

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Table II. Chromium(VI) Oxidations of Alkynes

alkyne	Cr(VI) reagent	solvent	reaction time, h	% of unreacted $RC{\equiv}C\text{-}CH_2R'$	% of $RC(O)C\text{-}(O)CH_2R'$	% of RCO_2H	% of $RC{\equiv}C\text{-}C(O)R'$
diphenylethyne	CrO_2Cl_2	H_2CCl_2	0.5	3	35	62	
	$CrO_2(O\text{-}t\text{-}Bu)_2$	C_5H_{12}	336	100	0	trace	
	$CrO_2(O\text{-}t\text{-}Bu)_2$	$(CH_3)_3COH$	74	96	3	1	
	CrO_3/C	$C_6H_5CH_3$	167	100	0	0	
	$CrO_3(C_5H_5N)_2$	H_2CCl_2	24	99	1	trace	
1-phenyl-1-propyne	CrO_2Cl_2	H_2CCl_2	0.5	5	5	82	8
	$CrO_2(O\text{-}t\text{-}Bu)_2$	$(CH_3)_3COH$	74	62	0	38	0
	$CrO_2(O\text{-}t\text{-}Bu)_2$	H_2CCl_2	284				2
	$CrO_2(O_2CCH_3)_2$	$(CH_3CO)_2O$	0.25	28	72	0	0
	CrO_3/C	$C_6H_5CH_3$	167	100	0	0	0
	$CrO_3(C_5H_5N)_2$	H_2CCl_2	24	99	0	0	1
	$CrO_3(C_5H_5N)_2$	H_2CCl_2	118				60
	$C_5H_5NHCrO_3Cl$	H_2CCl_2	380				trace
1-phenyl-1-butyne	CrO_2Cl_2	H_2CCl_2	0.5	36	40	8	16
	$CrO_2(O\text{-}t\text{-}Bu)_2$	$(CH_3)_3COH$	74	42	1	55	2
	$CrO_2(O\text{-}t\text{-}Bu)_2$	H_2CCl_2	284				2
	$CrO_2(O_2CCH_3)_2$	$(CH_3CO)_2O$	0.25	36	38	28	6
	$CrO_3(C_5H_5N)_2$	H_2CCl_2	24	100	0	0	trace
	$CrO_3(C_5H_5N)_2$	H_2CCl_2	118				3
	$C_5H_5NHCrO_3Cl$	H_2CCl_2	380				5
2-decyne	$CrO_2(O\text{-}t\text{-}Bu)_2$	H_2CCl_2	284				trace
	$CrO_3(C_5H_5N)_2$	H_2CCl_2	118				10
	$C_5H_5NHCrO_3Cl$	H_2CCl_2	380				trace
5-decyne	$CrO_2(O\text{-}t\text{-}Bu)_2$	H_2CCl_2	284				trace
	$CrO_3(C_5H_5N)_2$	H_2CCl_2	118				60
	$C_5H_5NHCrO_3Cl$	H_2CCl_2	380				3
4-octyne	$CrO_2(O\text{-}t\text{-}Bu)_2$	H_2CCl_2	284				trace
	$CrO_3(C_5H_5N)_2$	H_2CCl_2	118				25
	$C_5H_5NHCrO_3Cl$	H_2CCl_2	380				2
7-tetradecyne	$CrO_2(O\text{-}t\text{-}Bu)_2$	H_2CCl_2	284				trace
	$CrO_3(C_5H_5N)_2$	H_2CCl_2	118				20
	$C_5H_5NHCrO_3Cl$	H_2CCl_2	380				5

reagent was brought to temperature in a thermostated water bath and vigorously stirred while the alkyne (0.005 mol) was added. The reaction was halted by adding 2% sodium bisulfite (50 mL) to the reaction mixture. The mixture was extracted three times with diethyl ether (35 mL). The combined ether extracts were washed with water (50 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure on a Büchi Rotavapor.

Chromyl Chloride in Methylene Chloride. A solution of freshly distilled chromyl chloride (1.04 g, 0.0067 mol) in anhydrous methylene chloride (5 mL) was added dropwise to a vigorously stirred solution of the alkyne (0.005 mol) in anhydrous methylene chloride (10 mL). The reaction mixture was maintained at 50 °C in a thermostated water bath for 30 min. The reaction was halted by adding zinc dust (0.5 g). After 5 min, water (50 mL) was added and the reaction mixture worked up as in the previous chromic acid reaction.

***tert*-Butyl Chromate in *tert*-Butyl Alcohol.** Chromium trioxide (3.3 g, 0.033 mol) was added to cold anhydrous *tert*-butyl alcohol (7.4 g, 0.1 mol). Pentane (50 mL) was added after the reaction was complete and the resulting solution dried over anhydrous sodium sulfate. The pentane solvent was removed under reduced pressure on a Büchi Rotavapor and *tert*-butyl alcohol (20 mL) added to the residue. The reagent was thermostated in a water bath at 50 °C and the alkyne (0.005 mol) added to the stirred solution. The reaction was halted after 74 h by cooling in ice and adding cold water (25 mL). The excess chromium(VI) reagent was reduced by adding oxalic acid (4.5 g) and the solution stirred until the bubbling ceased. Concentrated sulfuric acid (5 mL) was added and the reaction mixture extracted with three portions (35 mL) of diethyl ether. The combined ether extracts were washed with water (50 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure.

***tert*-Butyl Chromate in Pentane.** The method is identical with the previous procedure except that the pentane solvent was not removed under reduced pressure and additional *tert*-butyl alcohol was not added. Due to this reagent's reduced reactivity, the reaction was run for 2 weeks.

Chromium Trioxide on Graphite (Seloxcette Reagent). Anhydrous toluene (15 mL), Seloxcette reagent (Alpha Division of Ventron Corp., 5 g, 0.029 mol), and the alkyne (0.005 mol) were combined and the mixture refluxed for 167 h. The reaction was halted by adding water (20 mL) and extracted with three portions (20 mL) of diethyl ether. The remaining workup was identical with that used for the chromic acid reactions.

***tert*-Butyl Chromate in Methylene Chloride (2e).** Anhydrous *tert*-butyl alcohol (25 mL), pyridine (32 mL), and methylene chloride (480 mL) were combined, and the solution was cooled to −78 °C with dry ice. A solution of chromyl chloride (10.8 mL) in carbon tetrachloride (60 mL) was added at a rate which did not allow the temperature to rise above −70 °C. The reagent was allowed to slowly warm to room temperature during which time a precipitate of pyridinium chloride was formed. The resulting solution (80 mL) was combined with the alkyne (0.01 mol) and allowed to react for two weeks in a sealed flask.

Anhydrous diethyl ether (200 mL) was added to the reaction mixture. After the mixture was left to stand for 10 min, the liquid phase was decanted from the red-brown residue and the residue washed with three portions (50 mL) of ether. The combined ether solutions were passed through a column of Florisil (60–120 mesh, 50 g), and the eluate was concentrated (~50 mL) under reduced pressure using a Büchi Rotavapor. The residual pyridine was extracted with dilute hydrochloric acid, the ether solution dried over anhydrous sodium sulfate, and the remaining ether solvent removed under vacuum.

Chromyl Acetate in Acetic Anhydride. Chromium trioxide (0.67 g, 0.0067 mol) was added to freshly distilled acetic anhydride (25 mL) and the solution thermostated at 25 °C in a water bath. The alkyne (0.005 mol) was added to the stirred chromyl acetate solution. The reaction was halted after 15 min by adding 2% sodium bisulfite solution (50 mL), and the reaction mixture was

worked up, using the previously described procedure used for the chromic acid reactions.

Chromium Trioxide–Pyridine Complex. The reagent was prepared by the method reported by Dauben, Lorber, and Fullerton.[7] The resulting chromium trioxide–pyridine complex (39 g, 0.22 mol) was combined with a solution of the alkyne (0.01 mol) in anhydrous methylene chloride (300 mL) and the mixture allowed to react at 25 °C for 5 days. Anhydrous diethyl ether (200 mL) was added to the reaction mixture, mixed thoroughly, and allowed to stand for 10 min. The solution was decanted from the dark-brown residue, and the residue was washed with three portions (50 mL) of diethyl ether. The combined ether solutions were passed through a column of Florisil (60–200 mesh, 50 g), and the eluate was concentrated (~50 mL) under reduced pressure, using a Büchi Rotavapor. The residual pyridine was extracted with dilute hydrochloric acid, the ether solution dried over anhydrous sodium sulfate, and the remaining ether solvent removed under vacuum.

Pyridinium Chlorochromate in Methylene Chloride (2f). The alkyne (0.01 mol) was added to a mixture of pyridinium chlorochromate (Aldrich Chemical Co., 21.5 g, 0.02 mol) and anhydrous methylene chloride (200 mL), the flask sealed, and the mixture stirred at room temperature for 2 weeks. Anhydrous diethyl ether (200 mL) was added to the reaction mixture, and after 10 min the liquid phase was decanted from the red-brown residue. The residue was washed with three portions (50 mL) of diethyl ether and the combined ether solutions passed through a column of Florisil (60–200 mesh, 50 g). The solvent was removed under reduced pressure on a Büchi Rotavapor.

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Registry No. Diphenylethyne, 501-65-5; 1-phenyl-1-propyne, 673-32-5; 1-phenyl-1-butyne, 622-76-4; 2-decyne, 2384-70-5; 5-decyne, 1942-46-7; 4-octyne, 1942-45-6; 7-tetradecyne, 35216-11-6; diphenylethanedione, 134-81-6; benzoic acid, 65-85-0; 1-phenyl-1,2-propanedione, 579-07-7; 3-phenyl-2-propynal, 2579-22-8; 1-phenyl-1,2-butanedione, 3457-55-4; 4-phenyl-3-butyn-2-one, 1817-57-8; 2-decyn-4-one, 34695-28-8; 5-decyn-4-one, 13882-01-4; 4-octyn-3-one, 7299-56-1; 7-tetradecyn-6-one, 71328-65-9; chromic acid, 7738-94-5; chromyl chloride, 14977-61-8; *tert*-butyl chromate, 1189-85-1; chromium trioxide, 1333-82-0; chromyl acetate, 4112-22-5; pyridinium chlorochromate, 20492-50-6.

Selective Palladium-Catalyzed Vinylic Substitutions with Bromoiodo Aromatics

Joseph E. Plevyak, James E. Dickerson, and Richard F. Heck*

Department of Chemistry, University of Delaware, Newark, Delaware 19711

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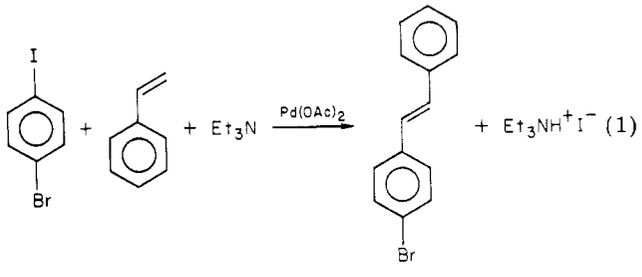
Palladium acetate catalyzed vinylic arylation of olefins occurs selectively at the iodo group of arenes containing both iodo and bromo substituents. Aryl bromides are reactive only if a triarylphosphine is added to the palladium acetate catalyst.

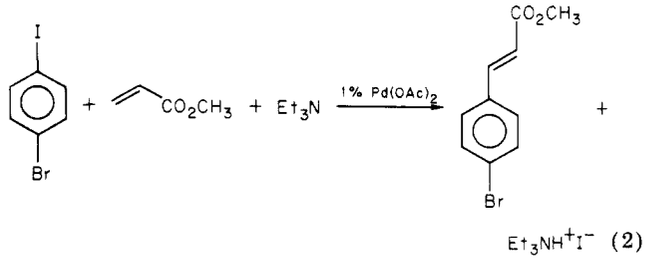
The palladium-catalyzed aryl halide reaction with olefins provides a convenient method for the preparation of 1-aryl olefins.[1] The catalyst required for the reaction depends upon the halide present; aryl iodides require only palladium acetate while aryl bromides do not react unless a triarylphosphine is also present. Therefore, it appeared possible that reactants containing both iodo and bromo groups could be caused to undergo reaction either at the iodo position or at both halo positions. This proved to be possible, and some examples of the reaction are reported herein.

Results and Discussion

4-Bromoiodobenzene is easily prepared by the bromination of iodobenzene.[2] This compound reacts with styrene in the presence of triethylamine and 1 mol % palladium acetate, based upon the organic halide, with acetonitrile as solvent at 100 °C in 17 h to form (*E*)-4-bromostilbene in 64% yield (eq 1). (All yields reported are of purified products.) Similarly, 4-bromoiodobenzene and methyl acrylate react to form (*E*)-methyl 4-bromocinnamate in 5.5 h at 100 °C in 68% yield (eq 2). Further reaction of this



compound with styrene in the presence of a 1% palladium acetate–2% tri-*o*-tolylphosphine catalyst with triethylamine as base produces (*E,E*)-methyl 4-styrylcinnamate in 63% yield (eq 3).



2-Bromoiodobenzene, prepared by the Sandmeyer reaction from 2-bromoaniline, reacted selectively with acrylic

(1) C. B. Ziegler and R. F. Heck, *J. Org. Chem.*, **43**, 2941 (1978), and references therein.
(2) H. Hirtz, *Chem. Ber.*, **29**, 1405 (1896).

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