Reduction of Acetylenes by Chromium(II)-Amine Complexes[1]

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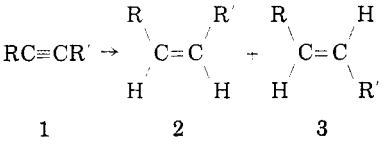
Received February 20, 1979

Alkylphenylacetylenes are reduced to the corresponding olefins by Cr(II)-amine complexes with a very high stereoselectivity for the cis isomer. Terminal acetylenes are likewise reduced, but dialkylacetylenes are not reactive to these reagents. The relative efficiencies of the Cr(II) complexes from several amines have been compared. Substituted propargyl alcohols are converted to allylic alcohols by the Cr(II) reagents, but in this instance mixtures of the cis and trans isomers are obtained. The product ratios depend on the nature of the substitution on the propargyl alcohol and on the particular amine used to prepare the reagent.

In conjunction with a study of the free-radical cyclizations of acetylenic alkyl halides[2] promoted by chromous perchlorate-ethylenediamine [Cr^{II}en],[3] it was discovered that 1-phenyl-1-butyne was reduced with very high stereoselectivity to *cis*-1-phenyl-1-butene by this reagent. Prior work had indicated that reductions of acetylenes by Cr(II) species were limited to more activated substrates (i.e., terminal and conjugated acetylenes as well as those possessing a proximal hydroxyl, carboxyl, etc.).[4,5] Furthermore, these reactions displayed a propensity for the formation of trans olefins. Consequently we were prompted to examine the behavior of the Cr^{II}en reagent with a number of acetylenes in order to evaluate the scope and synthetic potential of this reduction.



1 2 3

The reduction of a series of acetylenes (see Table I) was performed by reacting the acetylene with a reagent prepared by the *rapid* addition of an aqueous solution of chromous perchlorate to a cold solution of ethylenediamine in DMF under an argon atmosphere. This addition is exothermic causing the temperature of the reaction mixture to rise to ~15 °C. The reagent was allowed to warm to room temperature prior to adding the alkyne. The ensuing reaction was followed by GLC monitoring of aliquots. The homogeneous solution changes from blue-violet to deep purple upon addition of the acetylene and then gradually turns the characteristic reddish violet color of Cr(III) in this medium as the reaction proceeds. The products were identified by GLC isolation and spectral characterization. The cis olefins **2** were the only products observed from 1-phenyl-1-alkynes **1a-c**. In particular, the corresponding trans olefins **3** were not found. In the case of **1a** the amount of trans olefin in the product was shown to be less than 1% by GLC comparison with an authentic sample of *trans*-1-phenylpropene (prepared by reduction of **1a** with lithium aluminum hydride in refluxing THF).[6]

A problem with the reaction of **1a** is that only 60% conversion was observed when 4 mmol of acetylene was treated with 10 mmol of Cr(II) and 45 mmol of ethylenediamine. Comparable results were obtained with homologues **1b** and **1c**. However, a reaction using the same quantities of reagents with 2 mmol of **1a** did give a 96% conversion to **2a** (82% isolated yield). The ethylenediamine is a necessary component of the reagent as demonstrated by the lack of reduction when this material is omitted. Decreasing the amount of amine decreased the conversion of **1a**, whereas adding more of this ingredient increased the extent of reduction (see Table I). Curiously, preparation of the reagent by slow addition of the aqueous Cr(II) solution to the amine in DMF in such a manner that the temperature did not rise above 5 °C led to an inactive reagent, a result which was repeated with each of the acetylenes **1a**, **1b**, and **1c**. Furthermore, a reagent prepared by adding the ethylenediamine to a preformed solution of Cr(II) in DMF gave essentially no reduction of **1a**. Finally, increasing the reaction temperature to 50 °C after addition of the acetylene **1b** lowered the conversion substantially.

The key role of ethylenediamine in promoting the Cr(II) reduction of these acetylenes suggested a survey of other amines. The amines utilized all gave heterogeneous brown suspensions which were, nonetheless, effective in converting **1a** to **2a**. The reduction of 1.7 mmol of acetylene with 10 equiv of Cr(II) gave the following conversions: ethylamine (78%), cyclohexylamine (96%), *tert*-butylamine (92%), and triethylamine (100%). A series of reactions using varying amounts of triethylamine demonstrated a maximum in the percentage conversion of **1a** at roughly four amines per Cr(II); additional amine lowers the efficiency. The $Cr^{II}Et_3N$ reagent is also dramatically affected by the temperature of its preparation as indicated by the following conversions from the same quantities of reagents mixed at the indicated temperatures: -16 °C (37%), 15 °C (58%), 37 °C (23%).

Diphenylacetylene (**1d**) was reduced quantitatively to *cis*-stilbene by 2.5 equiv of the $Cr^{II}Et_3N$ reagent. The Cr^{II}en reagent was equally selective, although somewhat less effective (84% conversion). Omission of the amine resulted in recovery of the starting material.

Terminal acetylenes, which are reduced by aqueous chromous ion,[4,7] are quite reactive to the Cr(II)-amine reagents. Thus, 1-hexyne (**1e**) is converted almost completely to 1-hexene by a slight excess of Cr^{II}en. Phenylacetylene (**1f**) is rapidly and quantitatively reduced to styrene by this reagent. The stereochemistry of the latter reduction was investigated using phenylacetylene-2-*d* (**1g**). Reaction with 2.5 equiv of the Cr^{II}en reagent gave a 96% isolated yield of styrene-β-*d* which was estimated to be a 95:5 mixture of the cis/trans isomers by NMR.[8] Re-

(1) Support of this work by a research grant from the National Science Foundation is gratefully acknowledged.

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0022-3263/79/1944-3471$01.00/0

Table I. Reduction of Acetylenes to Olefins by Chromous Perchlorate in DMF

acetylene	R	R′	mmol	Cr(II), mmol	amine (mmol)	% conversion	
1a	Ph	CH_3	4	10	en (45)	60	
			2	10	en (45)	96	
			2	10		0	
			4	10	en (15)	52	
			4	10	en (35)	82	
			1	2.8	en (22)	1	(5 °C)[a]
			1	2.8	en (22)	60	(30 °C)[a]
			1.7	10	$EtNH_2$ (50)	78	
			1.7	10	c-$C_6H_{11}NH_2$ (60)	96	
			1.7	10	t-$BuNH_2$ (40)	92	
			1.7	10	Et_3N (60)	100	
			1	2.8	Et_3N (2.5)	43	
			1	2.8	Et_3N (5)	53	
			1	2.8	Et_3N (10)	60	
			1	2.8	Et_3N (15)	56	
			1	2.8	Et_3N (20)	50	
			1	2.8	Et_3N (25)	42	
			1	2.8	Et_3N (50)	26	
			1	2.8	Et_3N (10)	37	(−16 °C)[a]
			1	2.8	Et_3N (10)	58	(15 °C)[a]
			1	2.8	Et_3N (10)	23	(37 °C)[a]
1b	Ph	C_2H_5	2	5	en (22)	60	
			2	5	en (22)	22	(50 °C)[b]
			1	5	en (22)	<1	(5 °C)[a]
1c	Ph	n-C_3H_7	2	5	en (22)	58	
			2	5	en (22)	<1	
1d	Ph	Ph	2	5	en (15)	84	
			2	5	Et_3N (30)	100	
			2	5		0	
1e	n-C_4H_9	H	2.4	5	en (22)	96	
1f	Ph	H	1	5	en (22)	100	
			1	5		<5	
1g	Ph	D	2	5	en (22)	100	(95:5)[c]
			2	5	Et_3N (30)	100	(90:10)[c]
			2	5	en (22)	100	(70:30)[c,d]
1h	C_2H_5	C_2H_5	2	5	en (22)	0	
			2	5	Et_3N (30)	0	

[a] Reagent prepared at the indicated temperature. [b] Reaction was heated at the indicated temperature after mixing. [c] Ratio of **2g**/**3g** as determined by NMR. [d] THF solvent

duction of **1g** with the $Cr^{II}Et_3N$ reagent also proceeded rapidly, although somewhat less stereoselectively (90:10 ratio). Replacing the DMF solvent by THF resulted in an active Cr^{II}en reagent, but reduction was appreciably less stereoselective, a 70:30 ratio of *cis*- to *trans*-styrene-β-*d* being obtained. In our hands, neither aqueous chromous perchlorate nor chromous sulfate gave more than 5% conversion of **1f** to product, thereby thwarting comparison of the stereoselectivity under these conditions. These results are puzzling in view of the report[4] that aqueous chromous ion reduces this acetylene, but this discrepancy only serves to underline the very critical nature of the reaction conditions for these Cr(II) reductions.

All attempts to extend the Cr(II)–amine reduction to dialkylacetylenes such as **1h** were unsuccessful.

Several further experiments were performed on 1-phenylpropyne in an attempt to obtain some mechanistic information concerning these reductions. Analysis for Cr(II) in an experiment in which 1.9 mmol of **1a** was 51% converted to **2a** with an initial 5.2 mmol of Cr^{II}en indicated that 3.4 equiv of Cr(II) had been consumed per acetylene reduced. This result emphasizes the higher than anticipated utilization of Cr(II) which was pointed out above. It was further shown that this inefficiency is not the result of hydrogen formation by reduction of water under the reaction conditions,[3,9] since no gas was evolved in the course of a functioning reduction. In another experiment, the reaction mixture was poured into an excess of D_2O after 1 h and then processed following an additional hour. This reduction had proceeded to 70% completion giving olefin **2a** which showed 75% d_0, 21% d_1, and 4% d_2 by mass spectrometric analysis. Deuterium NMR demonstrated that the label was approximately equally distributed between the two olefinic carbons.

Unfortunately, not much can be said with assurance concerning the mechanism of these acetylene reductions at this time. The high cis stereoselectivity is certainly suggestive of a metal hydride addition and the peculiarities concerning the preparation of a reactive reagent are consistent with a relatively unstable chromium intermediate being the active reducing species. However, the mode of formation and the exact nature of this intermediate species are rather obscure at present.

In contrast to the simple dialkylacetylenes, propargyl alcohols have been shown to undergo facile reduction by aqueous chromous salts to the corresponding *trans*-allylic alcohols.[4] In the present work 2-butyn-1-ol (**4a**) was

$$\underset{\mathbf{4}}{RC{\equiv}CCR^1R^2OH} \rightarrow \underset{\mathbf{5}}{RC(H){=}CCR^1R^2OH} - \underset{\mathbf{6}}{RC(H)(H){=}CCR^1R^2OH}$$

reduced quantitatively and stereoselectively to *trans*-crotyl alcohol (**5a**) by chromous perchlorate in DMF without added amine (Table II). The Cr^{II}en reagent gave 97% conversion to a 93:7 ratio of *trans*- to *cis*-crotyl alcohol (**6a**). Interestingly, the $Cr^{II}Et_3N$ reagent reversed the stereo-

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Table II. Reduction of Propargyl Alcohols by Chromous Perchlorate in DMF

propargyl alcohol								
no.	R_1	R_2	R_3	mmol	Cr(II), mmol	amine (mmol)	% conversion	5/6 ratio
4a	CH_3	H	H	1	5		100	100:0
				2	10	en (45)	97	93:7
				1.4	5	Et_3N (30)	79	19:81
4b	C_2H_5	H	H	2.4	5	en (23)	100	62:38
4c	n-C_3H_7	H	H	2	5	en (23)	100	55:45
				2	5	Et_3N (30)	100	10:90
4d	n-C_5H_9	H	H	1.8	5	en (23)	100	27:73
4e	Ph	H	H	0.9	5	Et_3N (30)	20	0:100
4f	CH_3	CH_3	H	2.3	5	Et_3N (30)	52	8:92
4g	CH_3	CH_3	CH_3	1.7	5	en (23)	30	20:80

selectivity leading to a 19:81 ratio of **5a/6a** (79% conversion). Increasing the chain length of the alkyl substituent of **4** increased the proportion of cis product obtained from the chromous–amine reductions. Thus, reduction of 2-pentyn-1-ol (**4b**) with Cr^{II}en gave complete conversion to a 62:38 ratio of **5b/6b**, 2-hexyn-1-ol (**4c**) yielded **5c** and **6c** in a 55:45 ratio, and 2-heptyn-1-ol (**4d**) produced a 27:73 ratio of **5d/6d**. Interestingly, **4c** was transformed by the $Cr^{II}Et_3N$ reagent into a mixture in which the cis alcohol was heavily favored over the trans isomer (**5c/6c** ratio of 10:90). This reagent also reduced 3-phenyl-2-propyn-1-ol (**4e**) with high stereoselectivity to *cis*-cinnamyl alcohol (**6e**).

Increasing substitution at the carbinol carbon decreases the conversion of starting material but appears to favor cis reduction; $Cr^{II}Et_3N$ gave 52% conversion of 3-butyn-2-ol (**4f**) to a 8:92 ratio of **5f/6f**, whereas Cr^{II}en converted 2-methyl-3-butyn-2-ol (**4g**) in 30% to a 20:80 mixture of **5g/6g**.

Thus, it appears that the reduction of propargyl alcohols by the Cr(II)–amine reagents proceeds by two competing processes, a trans reduction similar to the exclusive pathway which occurs in the absence of amine and a cis reduction like that observed for the phenylacetylenes. The relative proportions of these two competing reductions depend on both the nature of the propargyl alcohol and the amine.

Experimental Section

General. Nuclear magnetic resonance (NMR) spectra were recorded with Varian EM-360, HA-100, and HR-220 spectrometers on samples in CCl_4 solution. Infrared (IR) spectra were obtained with a Perkin-Elmer Model 137 Infracord spectrometer on liquid films. Mass spectra were recorded at 70 eV with AEI MS-9 and Varian MAT CH-7 spectrometers. Gas chromatography–mass spectrometry was performed with the CH-7 mass spectrometer interfaced to a Varian Model 1200 gas chromatograph. Analytical gas chromatography (GLC) was performed on Aerograph Model 600-D and Varian Model 1200 gas chromatographs. Analytical columns were: 10 ft × 0.125 in. of 15% Ucon polar on 60–80 Chromosorb W; 4 ft × 0.125 in. of 10% Carbowax 20 M on 60–80 Chromosorb W; 20 ft × 0.125 in. of 30% Carbowax 20 M on 60–80 Chromosorb W. Peak areas were used for percentage composition determinations and are uncorrected for individual compound response. Preparative GLC was performed on an Aerograph A90-P3 chromatograph utilizing a 10 ft × 0.250 in. column of 15% Ucon polar on 60–80 Chromosorb W. Anhydrous $MgSO_4$ and Na_2SO_4 were routinely used as drying agents.

Chromous Perchlorate.[10] Chromous perchlorate was prepared using chromium metal obtained from Poly Research Corp. (99.999% stated purity). Into a 300-mL, round-bottom, one-neck flask, equipped with a gas-inlet tube and a permanent side arm with a stopcock and rubber septum, was placed 200 mL of 2 N perchloric acid. This solution was degassed by bubbling argon through for 2 h. Chromium chips (14 g) were washed with concentrated HCl and rinsed several times with distilled water before addition to the perchloric acid solution under argon. The solution was stirred at 50 °C until the evolution of hydrogen ceased, usually about 12 h. The resulting ~1 M solution was stored under argon at room temperature. All transfers of this reagent were made by syringe.

Chromous Reductions. The chromous reagent typically used in the reduction of acetylenes involved dilution of the standard chromous perchlorate solution in the following manner: 10 mL of 1 M aqueous chromous perchlorate solution was added to a degassed solution of amine (ethylenediamine, triethylamine, etc.) in 30 mL of reagent grade DMF cooled in an ice bath. The resulting chromous reagent (~0.23 M) was allowed to warm to room temperature prior to use. The ethylenediamine reagent thus formed was a homogeneous violet solution; other amines produced brown suspensions. The concentration of chromium(II) could be determined by titration.[11]

A typical reduction involved the direct addition of the acetylene to this solution under argon. The mixture was stirred at room temperature until the product mixture showed no further change in composition (monitored by GLC analysis of aliquots quenched in 3 N HCl and extracted into ether). The reaction mixture was poured into a separatory funnel containing an excess of cold 3 N HCl covered by a layer of pentane or ether. The aqueous layer was extracted several times with additional solvent and the extracts were combined. The organic extract was washed successively with 3 N HCl, H_2O, $NaHCO_3$ solution, and H_2O. It was dried and concentrated and the residue was analyzed by GLC. Pure samples of the products were isolated by GLC and identified by comparison of spectra with those of authentic samples. The data for these routine experiments are given in Tables I and II. Additional experiments are described below.

Reduction of 1-Phenylpropyne (1a). To 10 mmol of the standard Cr^{II}en solution was added 232 mg (2 mmol) of **1a**. The reaction had proceeded to 96% conversion after 24 h. Isolation of the product by GLC yielded 190 mg (82%) of **2a**.

After 1 h a similar reaction was quenched by pouring into 50 mL of D_2O (98% D) covered by a layer of ether. GLC analysis indicated a 30:70 mixture of **1a/2a**. The D_2O layer was extracted several times with ether over a period of 1 h. Normal workup and isolation by preparative GLC yielded 114 mg (70%) of **2a**. The product was subjected to deuterium NMR analysis: ^2H NMR δ 5.96, 5.30 (relative to external Me_4Si-d_{12} reference) with approximately equivalent integrations. Analysis by mass spectrometry at 30 eV indicated approximately 76% d_0, 21% d_1, and 4% d_2.

A reduction was performed on **1a** by adding 220 mg (1.9 mmol) to a solution of 4 mL of 1.30 M chromous perchlorate and 1.5 mL (22 mmol) of ethylenediamine in 17 mL of DMF. After 24 h the reaction had stopped at a 49:51 ratio of **1a/2a**. Analysis of the final reaction mixture revealed that 3.38 mmol of chromous reagent had been consumed in the course of the reduction of 0.97 mmol of acetylene.

Hydrogen evolution during the course of the reduction was monitored by attaching a gas collection apparatus to the reaction flask. In the flask were placed the standard Cr^{II}en reagent and 232 mg (2 mmol) of **1a**. After 24 h no gas had been collected. GLC indicated a 20:80 mixture of **1a/2a**.

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A reaction was run using an alternate sequence of mixing the components. To 5 mmol of chromous perchlorate reagent in 20 mL of DMF was added 1.5 mL (23 mmol) of ethylenediamine. To this reagent was added 100 mg (1 mmol) of **1a**. Analysis after 24 h indicated only 4% conversion to **2a**.

***trans*-1-Phenylpropene (3a).**[6] To 1.0 g of $LiAlH_4$ suspended in 30 mL of THF was added 1.0 g of **1a**. The mixture was refluxed for 60 h, cooled, and quenched with 5 mL of saturated Na_2SO_4 solution. The organic layer was dried, filtered, and concentrated to yield a 23:7:70 mixture of **1a**/**2a**/**3a**. Isolation by preparative GLC yielded 600 mg (60%) of **3a**.

Reduction of 2-Butyn-1-ol (4a). A. To 10 mmol of Cr^{II}en reagent was added 140 mg (2 mmol) of **4a**. Analysis after 24 h showed a 3:90:7 mixture of **4a**/**5a**/**6a**. *trans*-Crotyl alcohol (**5a**) shows: NMR δ 5.65–5.25 (m, 2), 3.90 (m, 2), 3.25 (s, 1), 1.68 (d of d, 3, J = 3.5, 1.5 Hz). *cis*-Crotyl alcohol (**6a**) shows: NMR δ 5.65–5.25 (m, 2), 4.04 (d, 2, J = 5 Hz), 3.62 (s, 1), 1.63 (d, 3, J = 5 Hz).

The stability of the products was examined by subjecting a 59:41 mixture of **5a**/**6a** to the Cr^{II}en reagent. After 24 h the ratio was 58:42.

Phenylacetylene-2-*d* (1g).[12] To 30 mL of 1.6 M *n*-butyllithium in 50 mL of THF was added 4.0 g of **1f**. The mixture was refluxed for 1 h followed by the addition of 5 mL of D_2O (98% D). The THF layer was dried and concentrated to yield 3.7 g (93%) of **1g**. The IR and NMR showed no absorptions for the acetylenic hydrogen; the mass spectrum indicated ~98% isotopic purity: m/e (relative intensity) 104 (7.4), 103 (100.0), 102 (4.0), 77 (14.2), 76 (9.9).

Registry No. **1a**, 673-32-5; **1b**, 622-76-4; **1c**, 4250-81-1; **1d**, 501-65-5; **1e**, 693-02-7; **1f**, 536-74-3; **1g**, 3240-11-7; **1h**, 928-49-4; **2a**, 766-90-5; **2b**, 1560-09-4; **2c**, 7642-18-4; **2e**, 592-41-6; **2f**, 100-42-5; **2g**, 21370-59-2; **3a**, 873-66-5; **3d**, 103-30-0; **3g**, 6911-81-5; **4a**, 764-01-2; **4b**, 6261-22-9; **4c**, 764-60-3; **4d**, 1002-36-4; **4e**, 1504-58-1; **4f**, 27301-54-8; **4g**, 590-38-5; **5a**, 504-61-0; **5b**, 1576-96-1; **5c**, 928-95-0; **5d**, 33467-76-4; **5f**, 3899-34-1; **5g**, 71195-14-7; **6a**, 4088-60-2; **6b**, 1576-95-0; **6c**, 928-94-9; **6d**, 55454-22-3; **6e**, 71195-15-8; **6f**, 24652-50-4; **6g**, 71195-16-9; chromous perchlorate, 13931-95-8.

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Palladium(II)-Catalyzed Carboxylation Reactions of Olefins: Scope and Utility

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Received April 20, 1979

The palladium-catalyzed carbomethoxylation reaction of olefins, which takes place with methanol, carbon monoxide, stoichiometric amounts of cupric chloride as a reoxidant, and a sodium butyrate buffer, usually adds two carbomethoxy functions to the double bond. Thus, dimethyl succinate is obtained from ethylene. The product of the reaction of 1,5-hexadiene, however, depends on the carbon monoxide pressure. At 6 atm of carbon monoxide, dimethyl 2-(3-buten-1-yl)succinate was obtained while at 1-3 atm of carbon monoxide dimethyl 3,6-bis(carbomethoxy)octane-1,8-dioate was formed exclusively. The utility and the synthetic versatility of the carboxylation reaction was studied by using conjugated and nonconjugated, cyclic and acyclic diolefins. The carboxylation of various functionally substituted olefins such as unsaturated ketones, alcohols, and esters was carried out to determine the versatility of the dicarboxylation reaction. Generally the olefin function could be dicarboxylated in high yields.

The reaction of olefins with carbon monoxide in methanol to form esters can be effected in the presence of palladium(II) chloride (eq 1).[1] When a weak base such

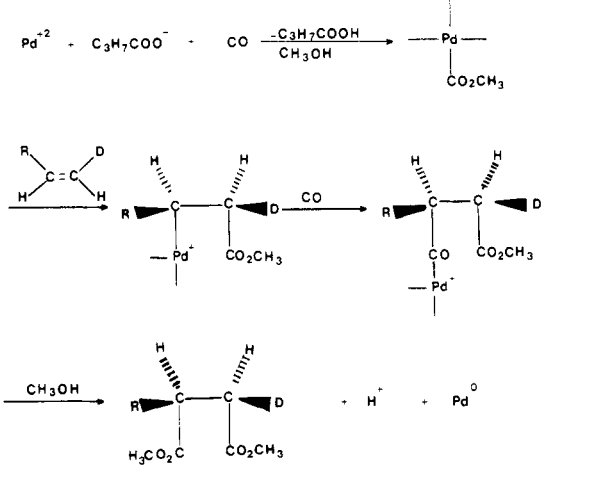
$$PdCl_2 + RCH{=}CH_2 + 2CO + 2CH_3OH \xrightarrow{C_3H_7CO_2Na} R(CO_2CH_3)CHCH_2CO_2CH_3 + Pd^0 + 2HCl \quad (1)$$

$$Pd^0 + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl \quad (2)$$

as sodium butyrate is present, a diester is formed under mild conditions (25 °C, 3 atm of CO). The reaction can be made catalytic with respect to palladium chloride by using stoichiometric amounts of cupric chloride as a reoxidant.[2]

The stereochemistry of the dicarboxylation reaction is cis and proceeds with the direct transfer of the carbomethoxyl group from the palladium to an olefinic carbon atom in a regiospecific anti-Markownikoff direction[2,3] (Scheme I). In the absence of a base a β-methoxy ester is obtained instead.

Scheme I



A palladium(II)-catalyzed reaction which produces diesters from olefins, carbon monoxide and alcohol under mild reaction conditions offers considerable synthetic potential. In order to determine the versatility of this reaction, we have studied the carboxylation of representative monoolefins, diolefins, and functionally substituted olefins.

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