Dicarboalkoxylation of Olefins and Acetylenes[1]

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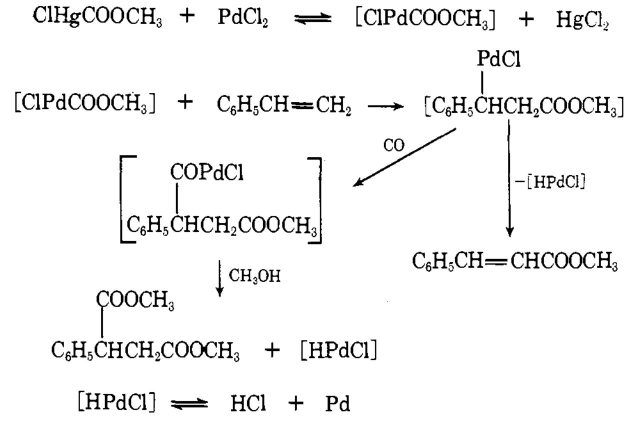
Abstract: A convenient procedure is described for converting olefins into substituted succinate esters and acetylenes into substituted maleate esters, by addition of two carboalkoxy groups to the unsaturated systems.

The monocarboalkoxylation of olefins with "carboalkoxypalladium salts" to form α,β-unsaturated esters was reported previously.[1,2] Since it was known that "alkylpalladium salts" could be carboalkoxylated in alcohol solution with carbon monoxide,[3] it seemed likely that the intermediate 2-carboalkoxyethylpalladium salts believed to be formed in the above reaction also could be carboalkoxylated and that a dicarboalkoxylation of the olefin might be possible. Indeed, a close examination of the products from the reaction of "carbomethoxypalladium chloride" (prepared *in situ* from $PdCl_2$ and $CH_3OCOHgCl$) with styrene revealed the presence of about 1% dimethyl phenylsuccinate as well as 10% of the expected methyl cinnamate. When the reaction was carried out under carbon monoxide, the yield of the diester increased sharply to 60% based upon the palladium chloride used. The reaction presumably takes the course shown in Scheme I.

Scheme I



There are literature reports that olefins (ethylene and propylene) can be dicarboalkoxylated directly with palladium chloride but under rather vigorous conditions (300–1200 psi and 120–150°),[4] and that styrene under laboratory conditions, in the presence of triethylamine and $PdCl_2$, can be dicarboxyalkylated but only in 7% yield.[5] Similarly, acetylene has been reported to undergo dicarbomethoxylation under mild conditions with a palladium chloride–thiourea catalyst, producing mainly dimethyl maleate along with some dimethyl fumarate and isomeric dimethyl muconates.[6] Our experiments indicate that this reaction is not as useful with higher acetylenes, however, because reaction rates are too slow. At higher pressures, Tsuji has shown that ethyl propiolate can be dicarboethoxylated but only in very low yield.[7]

In the absence of carbomethoxymercuric chloride, the required "carbomethoxypalladium chloride" is probably formed directly from carbon monoxide and the alcohol as is known to occur with mercuric acetate.[8]

$$PdCl_2 + CO + ROH \rightleftharpoons [ClPdCOOR] + HCl$$

Numerous related reactions have been demonstrated to occur with various transition metal carbonyls and alkoxides, for example[9]

$$Mn(CO)_4[P(C_6H_5)_3]_2^+ + CH_3O^- \longrightarrow CH_3OCOMn(CO)_3[P(C_6H_5)_3]_2$$

We have now examined the direct dicarboalkoxylation reaction and found that diesters can conveniently be prepared from a variety of olefins and acetylenes with carbon monoxide at low pressure, an alcohol, and palladium chloride, with or without mercuric chloride as a "cocatalyst."

Results and Discussion

The behavior of olefins in the dicarboalkoxylation reaction is quite different from that of acetylenes and therefore will be discussed separately.

Olefin Reactions. Styrene was found to react at 25° with carbon monoxide at 30 psi, methanol, and palladium chloride in 15 hr to form dimethyl phenylsuccinate in 25% yield based upon the palladium chloride used. In the presence of an equivalent amount of mercuric chloride, the yield increased to 86.5% with 11% methyl cinnamate also being formed. The mercuric chloride does not appear to be a reoxidant for the reduced palladium since increasing the relative amount of mercuric chloride above the stoichiometric amount relative to the palladium salt does not increase the yield of diester. The mercuric chloride, therefore, seems to be directly involved in the reaction in some unknown way. Cupric chloride reoxidizes only very slowly under the mild conditions used while it is much more effective at higher temperatures and pressures.[4] Lithium chloride or stannous chloride had no effect upon the yield of product. A variety of other olefins have been allowed to react under the mild conditions found most favorable for the styrene reaction using mercuric chloride as a cocatalyst. The results obtained are listed in Table I.

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[1] R. F. Heck, *J. Amer. Chem. Soc.*, 90, 5518 (1968).

[2] R. F. Heck, *ibid.*, 91, 6707 (1969).

[3] P. M. Henry, *Tetrahedron Lett.*, 2285 (1968).

[4] D. M. Fenton, U. S. Patent 3,397,226 (1968); G. Biale, U. S. Patent 3,530,168 (1970).

[5] T. Yukawa and S. Tsutsumi, *J. Org. Chem.*, 34, 738 (1969).

[6] G. P. Chiusoli, C. Venturello, and S. Merzoni, *Chem. Ind.* (*London*), 977 (1968).

[7] J. Tsuji and T. Nogi, *J. Org. Chem.*, 31, 2641 (1966).

[8] W. Schoeller, W. Schrauth, and W. Essers, *Ber.*, 46, 2864 (1913).

[9] T. Kruck and M. Noack, *Chem. Ber.*, 97, 1693 (1964).

Table I. Dicarboalkoxylation of Olefins and Acetylenes[a]

Olefin or acetylene (ml)	Palladium salt (mmol)	Mercury salt (mmol)	Solvent (ml)	Products[b]
$C_6H_5CH{=}CH_2$ (2)	$PdCl_2$ (5)	$ClHgCOOCH_3$ (5)	CH_3OH (10)	60% dimethyl phenylsuccinate 4% methyl cinnamate
$C_6H_5CH{=}CH_2$ (2)	$PdCl_2$ (4)	$HgCl_2$ (4)	CH_3OH (10)	86.5% dimethyl phenylsuccinate 11% methyl cinnamate
$C_6H_5CH{=}CH_2$ (2)	$PdCl_2$ (4)		CH_3OH (10)	25% dimethyl phenylsuccinate
$C_6H_5CH{=}CH_2$ (20)	$PdCl_2$ (50)	$HgCl_2$ (50)	C_2H_5OH (100)	48% diethyl phenylsuccinate 20% ethyl cinnamate
4-$CH_3C_6H_4CH{=}CH_2$ (10)	$PdCl_2$ (50)	$HgCl_2$ (50)	CH_3OH (100)	37% dimethyl 4-tolylsuccinate 15% methyl 4-methylcinnamate
4-$ClC_6H_4CH{=}CH_2$ (20 g)	$PdCl_2$ (50)	$HgCl_2$ (50)	CH_3OH (100)	39% dimethyl 4-chlorophenylsuccinate (80%) 21% methyl 4-chlorocinnamate (14%)
4-$CH_3OC_6H_4CH{=}CH_2$ (2)	$PdCl_2$ (4)	$HgCl_2$ (4)	CH_3OH (10)	20% methyl *p*-methoxycinnamate
trans-$C_6H_5CH{=}CHCH_3$[c] (2)	$PdCl_2$ (4)	$HgCl_2$ (4)	CH_3OH (10)	3% dimethyl 1-phenyl-1,2-propanedicarboxylate (isomer A) 72% dimethyl 1-phenyl-1,2-propanedicarboxylate (isomer B)
cis-$C_6H_5CH{=}CHCH_3$[c] (2)	$PdCl_2$ (5)	$HgCl_2$ (5)	CH_3OH (10)	14% dimethyl 1-phenyl-1,2-propanedicarboxylate (isomer A) 25% dimethyl 1-phenyl-1,2-propanedicarboxylate (isomer B)
c-C_5H_8 (2)	$PdCl_2$ (5)	$HgCl_2$ (5)	CH_3OH (10)	3% methyl cyclopentanecarboxylate 36% *cis*-dimethyl 1,2-cyclopentenedicarboxylate 43% dimethyl cyclopentenedicarboxylate (unknown isomer)
c-C_6H_{10} (20)	$PdCl_2$ (50)	$HgCl_2$ (50)	CH_3OH (100)	63% *trans*-methyl 2-methoxycyclohexanecarboxylate 6% *cis*-dimethyl 1,2-cyclohexenedicarboxylate
$CH_3(CH_2)_3CH{=}CH_2$ (20)	$PdCl_2$ (50)	$HgCl_2$ (50)	CH_3OH (100)	20% dimethyl 1,2-hexanedicarboxylate 72% methyl 2-methoxyheptanoate
trans-$CH_3CH_2CH{=}CHCH_2CH_3$ (20)	$PdCl_2$ (50)	$HgCl_2$ (50)	CH_3OH (100)	49.8% dimethyl 3,4-hexanedicarboxylate (*dl* isomer)
cis-$CH_3CH_2CH{=}CHCH_2CH_3$ (2)	$PdCl_2$ (5)	$HgCl_2$ (5)	CH_3OH (10)	16% methyl 3-methoxy-4-hexanecarboxylate 5% dimethyl 3,4-hexanedicarboxylate (meso isomer) 30% dimethyl 3,4-hexanedicarboxylate (*dl* isomer)
trans-$CH_3(CH_2)_2CH{=}CHCH_3$ (2)	$PdCl_2$ (5)	$HgCl_2$ (5)	CH_3OH (10)	55% dimethyl 2,3-hexanedicarboxylate
$C_6H_5C{\equiv}CH$ (2)	$PdCl_2$ (4)	$HgCl_2$ (4)	CH_3OH (10)	134% dimethyl phenylmaleate 8% methyl 3-chloro-3-phenylacrylate
$C_6H_5C{\equiv}CH$ (2)	$PdCl_2$ (4)		CH_3OH (10)	69% dimethyl phenylmaleate 9% methyl 3-chloro-3-phenylacrylate
$C_6H_5C{\equiv}CH$ (2)	$PdCl_2$ (5)	$HgCl_2$ (5)	$(CH_3)_2CHOH$ (10)	5% isopropyl 3-chloro-3-phenylacrylate (?) 160% diisopropyl phenylmaleate 62% phenylmaleic anhydride
$C_6H_5C{\equiv}CH$ (2)	$PdCl_2$ (5)	$HgCl_2$ (5)	CH_3COCH_3 (9) H_2O (1)	86%[e] (55%)[d] phenylmaleic anhydride
$C_6H_5C{\equiv}CCH_3$ (2)	$PdCl_2$ (5)	$HgCl_2$ (5)	CH_3OH (10)	156% dimethyl 1-phenyl-1,2-propenedicarboxylate 53% *trans*-methyl 3-chloro-2-methylcinnamate 10% *cis*-methyl 3-chloro-2-methylcinnamate
$CH_3(CH_2)_4C{\equiv}CH$ (2)	$PdCl_2$ (5)	$HgCl_2$ (5)	CH_3OH (10)	44% *trans*-dimethyl *n*-butylmaleate 183% *cis*-dimethyl *n*-butylmaleate
$CH_3CH_2C{\equiv}CCH_2CH_3$ (2)	$PdCl_2$ (5)	$HgCl_2$ (5)	CH_3OH (10)	134% dimethyl 3-hexene-3,4-dicarboxylate
$(CH_3)_3CC{\equiv}CH$ (2)	$PdCl_2$ (5)	$HgCl_2$ (5)	CH_3OH (10)	20% methyl 3-chloro-4,4-dimethyl-2-pentenoate 180% dimethyl 3,3-dimethyl-1,2-(1-butenedicarboxylate)

[a] Carried out at 25° with 30 psig of carbon monoxide for about 15 hr. [b] Yields based upon $PdCl_2$ used. [c] Reaction carried out at 50°. [d] Yield of isolated purified product. [e] Yield of crude product.

The yields and products from the dicarboalkoxylation reaction were found to be quite dependent upon the structure of the olefin. The 4-methyl- and 4-chlorostyrenes at 25° gave only about 38% yields of diesters along with 15–21% of the substituted cinnamate esters. The 4-methoxystyrene produced 20% of methyl 4-methoxycinnamate with only traces of the diester being formed. *trans*-Propenylbenzene at 25° gave the expected diester in 20% yield while the cis isomer gave very little product. At 50° yields increased significantly. The trans isomer gave a 72% yield of diester while the cis isomer gave 25% of the same diester and 14% of an isomeric diester. Cyclopentene gave 36% dimethyl *cis*-1,2- and 43% of an unknown cyclopentanedicarboxylate diester, not *trans*-1,2- or -1,3- or *cis*-1,3-, along with 3% methyl cyclopentanecarboxylate. The latter compound probably arose by the known Pd–HCl catalyzed carboxylation.[10] Cyclohexene, on the other hand, gave methyl *trans*-2-methoxycyclohexanecarboxylate in 63% yield and 6% of the cis diester. 1-Hexene gave a mixture of dimethyl 1,2-hexanedicarboxylate (20%) and methyl 2-methoxyheptanoate (72%). *trans*-3- and -2-hexene gave the expected diesters in 49 and 55% yields, respectively. The dicarboxyalkylation of *cis*-3-hexene gave 10% of a methoxy ester, 5% of a new diester, and 30% of the same diester as *trans*-3-hexene produced. Comparison with known samples[11] showed the product from

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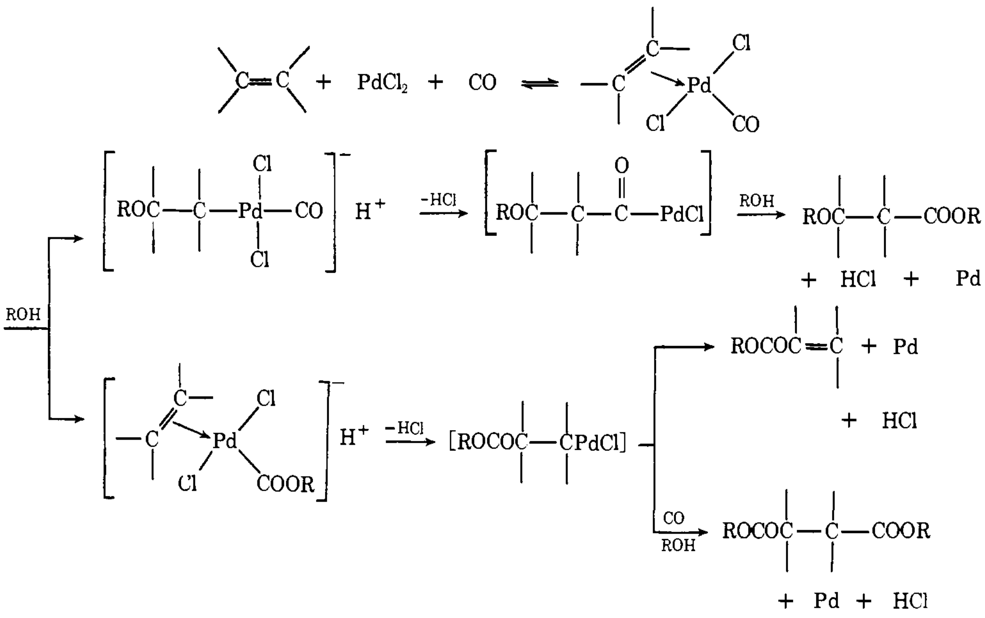
(10) J. Tsuji, M. Morikawa, and J. Kiji, *Tetrahedron Lett.*, 1437 (1963).

Scheme II



the *trans*-3-hexene to be the *dl* isomer of dimethyl 3,4-hexanedicarboxylate and the second diester from the *cis*-3-hexene was the meso isomer.

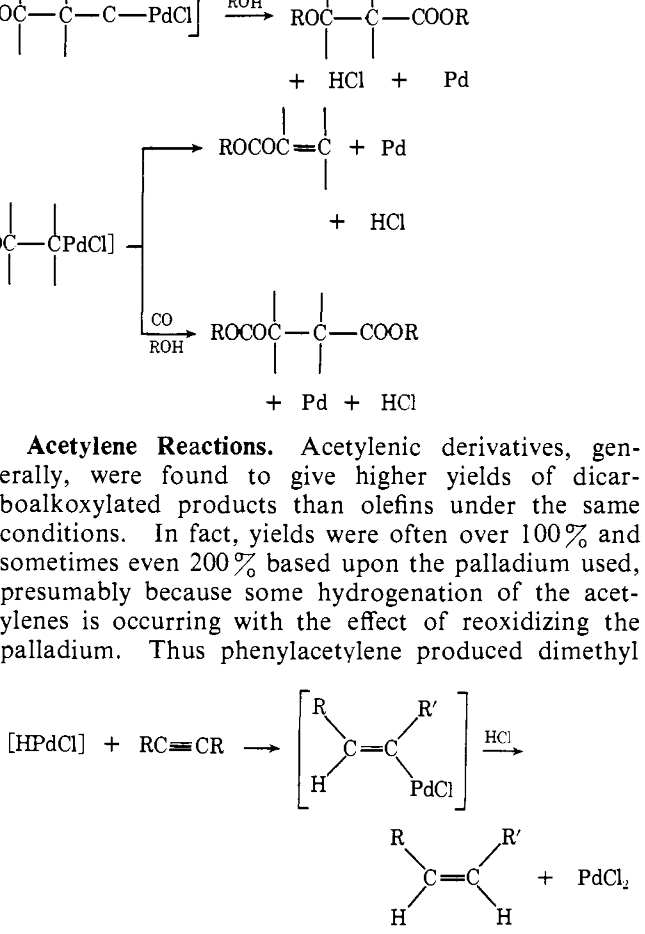
2-Alkoxy esters have been noted previously in palladium-catalyzed reactions of olefins with carbon monoxide and alcohols.[4] Probably there is a competition between coordinated olefin and carbon monoxide for the solvent alcohol, and the selectivity is very dependent upon the structure of the olefin. A reasonable explanation for these reactions is suggested in Scheme II. No doubt, varying carbon monoxide pressure and the reaction temperature will significantly affect relative proportions of the various possible products. The cinnamate ester products formed in the styrene dicarboalkoxylation may arise from alkoxy esters which lose alcohol during isolation.

The above mechanism would predict the cis addition of the two carboalkoxy groups. Since *cis*-propenylbenzene and *cis*-3-hexene, at least, gave isomeric mixtures of products, isomerization must occur, but it is not clear how this happens. *trans*-3-Hexene and, presumably, *trans*-propenylbenzene are producing only the *dl* diesters and the corresponding cis compounds are giving the meso isomers along with large amounts of the *dl* compounds. Olefin isomerization does not occur during the reaction and therefore cannot explain the cis–trans isomerization. Cyclopentene and cyclohexene, however, clearly give the cis diesters.

A possible explanation for the isomerization in the open-chain olefin reaction is that α,β-unsaturated esters are intermediates in the dicarboxylation and diesters are formed from them by [HPdCOOR] addition. Attempts to carboxylate methyl acrylate, crotonate, and cinnamate, however, were unsuccessful. Vinyl ether type products only were found. Thus, unsaturated esters, once formed, do not give diesters on further reaction under mild conditions.

Even though yields may not be high, the dicarboxyalkylation of olefins is a more convenient and much simpler method for preparing some derivatives of succinic acid than the previously known methods.

Acetylene Reactions. Acetylenic derivatives, generally, were found to give higher yields of dicarboalkoxylated products than olefins under the same conditions. In fact, yields were often over 100% and sometimes even 200% based upon the palladium used, presumably because some hydrogenation of the acetylenes is occurring with the effect of reoxidizing the palladium. Thus phenylacetylene produced dimethyl phenylmaleate in 134% yield along with 8% of methyl 3-chloro-3-phenylacrylate and smaller amounts of methyl cinnamate and methyl propiolate. Similarly, 1-phenyl-1-propyne, 1-hexyne, and 3-hexyne gave the expected diesters in at least 100% yields based upon the palladium chloride used. The products from the 1-phenyl-1-propyne and 3-hexyne are apparently isomerically pure and are presumably the cis isomers because the reaction of phenylacetylene in aqueous acetone solution produced phenylmaleic anhydride as the major product (86% yield). Treatment of the anhydride with methanol and diazomethane gave the same cis diester as was obtained by the direct reaction in methanol solution alone. The 1-hexyne reaction produced a 2:5 mixture of trans:cis diesters. The results of these reactions are summarized in Table I. The acetylenic reactions can be made catalytic at room temperature using oxygen and cupric chloride as reoxidants. Increasing the cupric chloride concentration above about 0.5 *M*, however, causes an increasingly important side reaction forming chloro esters. Two significant by-products observed in the 1-phenyl-1-propyne dicarboxylation reaction were chloro esters, probably isomeric methyl 3-chloro-2-methylcinnamates. The nmr spectra suggested the products were 53% of



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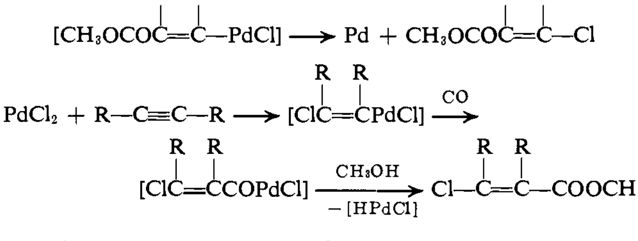
(11) H. Wren and J. Crawford, *J. Chem. Soc.*, 230 (1937).

the trans isomer and 10% of the cis isomer based upon the $PdCl_2$ used. The dicarboxyalkylation of 3,3-dimethyl-1-butyne also gave 20% of an unsaturated chloro ester. Presumably, the chloro esters are formed either by a reductive elimination of Pd(0) from the monocarboalkoxylated intermediate or by $PdCl_2$ addition followed by carbonylation and alcoholysis (Scheme III).

Scheme III

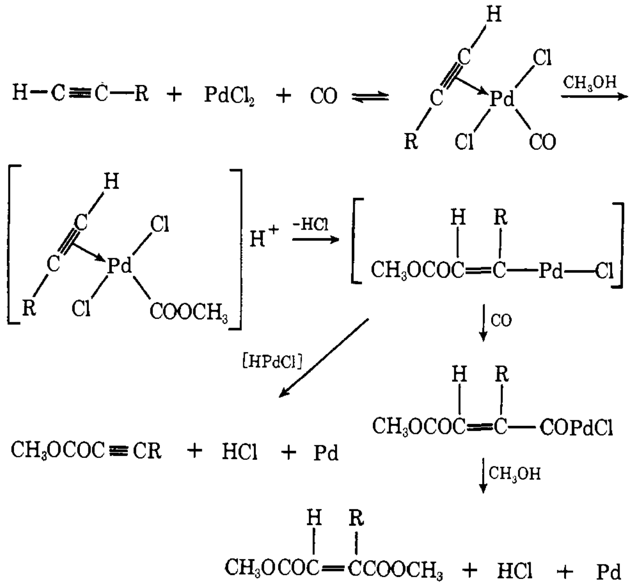


It is interesting that olefins produce only methoxy esters and acetylenes form only chloro esters as side products under the same reaction conditions.

Polar substituents on the unsaturated carbons may produce substantial deactivating effects on both the olefin and acetylene reactions. Acrylate and propiolate esters and the corresponding nitriles, for example, gave very little of the dicarboalkoxylated products under the usual conditions. Nevertheless, it is clear that a variety of olefinic and acetylenic compounds can be converted into dicarboalkoxylated derivatives easily, under normal laboratory conditions, by means of this reaction.

Carboxyalkylation, Methylation, and Arylation of Acetylenes. The fact that minor amounts of methyl phenylpropiolate were formed in the phenylacetylene dicarboalkoxylation reaction suggested that some elimination of [HPdCl] must be occurring from the intermediate monocarboalkoxylated vinylpalladium compound. The reactions in Scheme IV are probably involved. The major difficulty with this explanation is that a trans elimination of HPdCl is required, while in the carbomethoxylation of olefins, at least, a cis elimination seems probable.[2] Support for the proposed elimination is found in a study of the reaction of phenylacetylene with carbomethoxypalladium acetate, prepared by the exchange reaction of carbomethoxymercuric acetate with palladium acetate in the absence of carbon monoxide. The reaction produced methyl phenylpropiolate in 41% yield. The elimination does not appear to be base-catalyzed because the addition of tri-*n*-butylamine did not improve the yield. Using twice as much mercurial as palladium acetate produced the acetylenic ester in 82% yield based upon the palladium acetate used.

Scheme IV



$$C_6H_5C{\equiv}CH + CH_3OCOPdOAc \longrightarrow C_6H_5C{\equiv}CCOOCH_3 + HOAc + Pd$$

Unexpectedly, the same reaction carried out with chloride salts instead of acetates failed to produce any methyl phenylpropiolate. The probable explanation is that palladium chloride, coordinated with carbon monoxide, as in the phenylacetylene reaction, behaves like palladium acetate, while solvent coordinated palladium chloride is more reactive, probably polymerizing the acetylenes present.

The success of the carbomethoxylation suggested that methylation and arylation of acetylenes might also be possible. Indeed, the methylation of phenylacetylene with methylmercuric acetate gave a 26% yield of 1-phenyl-1-propyne, and phenylation with phenylmercuric acetate gave diphenylacetylene in 77% yield.

Experimental Section

Reagents. All the olefinic and acetylenic compounds used were obtained from commercial sources and were used without further purification. Carbomethoxymercuric chloride and acetate were prepared by the method of Schoeller, *et al.*[8]

General Procedure for Dicarboalkoxylation. The reactions were carried out in 300-ml, heavy-walled "Pyrex" bottles using magnetic stirring. The palladium and mercury salts were placed in the bottle with a magnetic stirring bar, and the bottle was capped with a self-sealing, neoprene rubber-lined metal cap having two small holes in the metal so that other materials could be added by means of "hypodermic" needles. The air in the bottle was replaced with carbon monoxide by evacuating on a pump and then pressuring several times with carbon monoxide through a needle. Generally, the bottle was then placed in a thermostated bath at 25°, the magnetic stirrer was started, and a solution of the olefin or acetylene in the alcohol was injected into the bottle containing about 10 psi of carbon monoxide. As soon as the solution had been added, the carbon monoxide pressure was raised to 30 psi and the reaction was continued under these conditions overnight. To obtain the highest yields in this reaction, good stirring and thorough mixing of the liquid and gas phases are essential.

Analyses were generally carried out by gas chromatography on a 6 ft Carbowax 20M on Chromosorb W column. Products were isolated by filtering the reaction mixtures through Celite, rinsing with more of the alcohol used as solvent to remove precipitated palladium metal, and then evaporating or distilling most of the alcohol from the product. The residue was dissolved in ether and the solution washed several times with water or aqueous sodium bicarbonate to remove mercury salts. After drying with anhydrous magnesium sulfate, the ether solution was distilled, first at atmospheric pressure to remove the solvent, and finally under reduced pressure. The products could be purified by careful distillation, but with the small quantities used, it was usually easier to distil without separation and make a final purification for analysis by preparative gas chromatography. In a few examples, products were made on a very small scale and isolation was by gas chromatography only. Analytical data, properties, and nmr spectra for the products prepared are given in Table II.[12]

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[12] Table II (which contains analytical data for reaction products) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-2712. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

The dimethyl phenylsuccinate was further purified by recrystallization from aqueous methanol. Phenylmaleic anhydride was isolated by sublimation from the reaction mixture and recrystallization from benzene–hexane rather than by distillation, and, of course, in this example, mercuric salts were removed only with water rather than with aqueous bicarbonate.

Identification of dimethyl *cis*-1,2-[13] and dimethyl *cis*-1,3-cyclopentenedicarboxylate[14] was made by nmr and glc comparison with authentic samples. Similarly methyl *trans*-2-methoxycyclohexanecarboxylate was prepared by treatment of the *trans*-2-hydroxycyclohexanecarboxylic acid[15] with freshly prepared silver oxide and iodomethane. *cis*-1,2-Cyclohexanedicarboxylic acid was commercially available from the Aldrich Chemical Co., and it was esterified with diazomethane to obtain an authentic sample. The authentic *dl* and meso dimethyl 3,4-hexanedicarboxylates were obtained by diazomethane treatment of the known acids.[12]

In carrying out reactions employing carbomethoxymercuric chloride significant pressure increases were noted. This reaction was therefore begun at 0° and allowed to warm up slowly, releasing pressure as necessary to keep the pressure at 30 psi.

Carbomethoxylation of Phenylacetylene. A mixture of 0.64 g (22 mmol) of carbomethoxymercuric acetate,[8] 10 ml of acetonitrile, and 2 ml of phenylacetylene was stirred magnetically in an ice bath, and 0.45 g (2 mmol) of powdered palladium acetate was added. The mixture was stirred at 0° for 30 min and then at room temperature overnight. Gas chromatographic analysis showed the solution to be 0.07 *M* in methyl phenylpropiolate. A slightly lower yield was obtained when the reaction was carried out with 0.5 ml of tri-*n*-butylamine present.

A similar reaction with 1.28 g (4 mmol) of carbomethoxymercuric acetate and with 0.5 ml of tri-*n*-butylamine gave 0.136 *M* methyl phenylpropiolate. A sample of product was isolated from this reaction mixture by preparative gas chromatography. The analysis and nmr spectra are listed in Table II.

Methylation of Phenylacetylene. The reaction was carried out exactly as in the preceding experiment, substituting 1.37 g (5 mmol) of methylmercuric acetate for the carbomethoxymercuric acetate and using 1.12 g (5 mmol) of palladium acetate. After the mixture was allowed to react overnight, gas chromatographic analyses showed the solution to contain 1.3 mmol of 1-phenyl-1-propyne. A sample was isolated by preparative gas chromatography and the analyses obtained are given in Table II.[10]

Phenylation of Phenylacetylene. A reaction was carried out as in the preceding experiment, employing 1.68 g (5 mmol) of phenylmercuric acetate in place of methylmercuric acetate. After reacting overnight, the solution was found to contain 3.84 mmol of diphenylacetylene. An isolated sample was found to be essentially identical with a known sample of diphenylacetylene.

Acknowledgment. Laboratory assistance was provided by Mr. A. G. Fleming and nmr spectra were taken by Mr. L. Haas.

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(13) W. H. Perkin, *J. Chem. Soc.*, 572 (1894).

(14) W. H. Perkin and H. A. Scarorough, *ibid.*, 119, 1405 (1921).

(15) J. Pascual, J. Sistare, and A. Regas, *ibid.*, 1943 (1949).

Oxidations of Hydroaromatic Systems. II. 2,3-Dichloro-5,6-dicyanobenzoquinone[1]

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Abstract: Aromatic stabilization in the transition state is used to develop a new approach to the study of one- and two-electron oxidations involving hydrogen transfer. 2,3-Dichloro-5,6-dicyanobenzoquinone is shown to react with tropilidene and 1,2,3-triphenylcyclopropene 10^4 to 10^5 times faster than with simple model compound. This high reactivity is interpreted by aromatic stabilization in the transition state of the rate-limiting step and considered as additional evidence for hydride ion transfer. The high reactivity of 1,4-dihydrobenzene is discussed and interpreted as suggesting the simultaneous removal of two hydrogen atoms.

A large number of oxidation processes include the breaking of carbon–hydrogen bonds in the rate-limiting step. A fundamental question is whether this reaction occurs as a one-electron oxidation involving the transfer of a hydrogen atom, or as a two-electron oxidation with the transfer of a hydride ion.

The distinction between hydrogen atom and hydride ion transfer in oxidation processes is by no means easy to establish. Attempts have been made to classify oxidizing agents as one- and two-electron reagents based on reaction with compounds like hydrazine[2] or sulfurous acid;[3] however, electron transfer processes in these reactions and hydrogen transfers in the oxidations of organic compounds are basically too different to allow any close analogy. The formation of free radicals in solution was often taken as a proof of hydrogen atom transfer;[4] however, very ambiguous results were frequently obtained. The magnitude of the kinetic isotope effect was predicted to be different for hydrogen and hydride transfers,[5] but this view is not generally shared and experimental support is lacking. Linear free energy relationships between oxidation and solvolytic processes were used to support the hydride ion transfer mechanism,[6] but the basic similarity between electronic effects in the two types of mechanisms leaves the argument not quite convincing. Similarities in relative rates between known free radical reactions and oxidation processes were suggested to support a hydrogen atom transfer,[7] but the

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(1) (a) Part I: P. Müller, E. Katten, and J. Roček, *J. Amer. Chem. Soc.*, 93, 7114 (1971); (b) support of this work by the U. S. Army Research Office (Durham) is gratefully acknowledged; (c) presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(2) R. E. Kirk and A. W. Browne, *J. Amer. Chem. Soc.*, 50, 337 (1928).

(3) W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 447 (1957).

(4) For instance, J. S. Littler and W. A. Waters, *ibid.*, 1299 (1959).

(5) C. G. Swain, R. A. Wiles, and R. F. Bader, *J. Amer. Chem. Soc.*, 83, 1945 (1961).

(6) F. Mareš, J. Roček, and J. Sicher, *Collect. Czech. Chem. Commun.*, 26, 2355 (1961).

(7) K. B. Wiberg and R. J. Evans, *Tetrahedron*, 8, 313 (1960).