that the methyl groups are not equivalent and that the quartet is due to the superposition of two $^{31}P-^{1}H$ coupling patterns. Due to the fast relaxation of the ^{27}Al nucleus, spin–spin coupling is not usually observed.[30] The alkyl region of the ^{1}H NMR spectrum of $[(Me_3SiCH_2)_2AlPPh_2]_2$ shows a singlet for the silicon methyl groups and an unsymmetrical quartet for the methylene groups at 90 MHz. Expansion reveals a shoulder on the side of the line at lowest field. At 60 MHz, the signal due to the aluminum methylene groups simplifies to a fairly symmetrical triplet with a coupling constant of 2.6 Hz. The spectrum is independent of concentration in the range 0.102–0.361 m. At these concentrations virtually all $(Me_3SiCH_2)_2AlPPh_2$ should be in the form of dimers, with nonequivalent aluminum alkyl groups. The alkyl region of the spectrum of $[Et_2AlPPh_2]_2$ shows the expected splitting pattern for an ethyl group; a triplet at δ 1.31 for the methyl groups and a quartet at δ 0.80 for the methylene groups. The coupling constants are 7 Hz for both absorbances and are independent of spectrometer frequencies. However, further splitting of the methylene quartet is also observed. At all spectrometer frequencies, the methylene quartet lines are considerably broader than those due to the methyl groups. Expansion of the quartet does not reveal any details. The phenyl resonances are not helpful in providing more information about any of the molecules. Two adjacent complex multiplets in the δ 7.7–7.1 region are observed. The complexity of these signals results from the overlap of the $^{1}H-^{31}P$ and $^{1}H-^{1}H$ coupling patterns for the ortho, meta, and para ring hydrogens. The splitting of the lines for hydrogens on carbon adjacent to aluminum in the dimers may be explained by the existence of nonplanar, four-membered aluminum–phosphorus rings. A nonplanar dimer has been observed for the solid-state structures of $[I_2BPPh_2]_2$[31] and $[Me_2AlN(i\text{-}Pr)H]_2$.[32] The alkyl groups on aluminum are not equivalent, and the hydrogens on the α-carbon atoms would be split by two equivalent phosphorus atoms giving rise to a triplet for each of the two types of alkyl groups. Long-range $^{31}P-^{1}H$ coupling is observed in other systems[33] but it has not been reported previously for other organoaluminum phosphides mainly because the NMR spectra have not been observed. The proposed structure is also consistent with the proton-decoupled ^{31}P NMR spectrum of $[Et_2AlPPh_2]_2$, which consist of a single absorption at δ 42.3 (downfield from H_3PO_4) for two equivalent phosphorus atoms.

Acknowledgment. This work was supported in part by the Office of Naval Research.

Registry No. $Al(CH_2SiMe_3)_2Br$, 85004-93-9; $Al(CH_2SiMe_3)_2H$, 85004-94-0; Me_3AlPPh_2H, 85004-96-2; Et_3AlPPh_2H, 85004-97-3; $(Me_3SiCH_2)_3AlPPh_2H$, 85004-98-4; $(Me_3SiCH_2)_2AlPPh_2$, 84537-82-6; Me_2AlPPh_2, 85004-95-1; Et_2AlPPh_2, 1024-73-3; THF, 109-99-9; CH_3CN, 75-05-8.

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Synthesis of Diynes, α,β-Unsaturated Monoacids, and Diacids by the Selective Palladium(0)-Catalyzed and Phase Transfer Catalyzed Reactions of Vinylic Dibromides

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Three new, mild, and highly selective phase-transfer reactions are described. Vinylic dibromides derived from aromatic aldehydes react with carbon monoxide, zerovalent palladium compounds as the metal catalyst, and a phase-transfer agent in a two-phase system (C_6H_6, 5 N NaOH) to give diynes in reasonable yields. α,β-Unsaturated monacids were the major or only products formed by using vinylic dibromides, derived from aliphatic aldehydes or ketones, as reactants. Dicarbonylation of all classes of vinylic dibromides to diacids occurred by using *tert*-amyl alcohol as the organic phase. Mechanisms are proposed for these selective transformations.

Phase-transfer catalysis has proved to be a useful method for effecting a number of reactions catalyzed by palladium complexes. For example, palladium bromide is a good catalyst for the phase transfer catalyzed synthesis of diphenyl carbonate from phenol, carbon monoxide, and oxygen (eq 1).[2] Halide displacement by cyanide ion can occur by using palladium(0) and crown ether catalysts.[3] The synthesis of aryl and alkenyl sulfides by displacement of halide by the thiolate ion is catalyzed by organopalladium(II) compounds under two-phase conditions (eq 2). A phase-transfer agent is not required in the latter reaction, although its presence improves the product yield in selected cases.[4] Phase transfer catalyzed isomerization[5]

$$2PhOH + CO + 0.5O_2 \xrightarrow[\substack{(n\text{-}C_4H_9)_4NBr,\ Mn(acac)_2 \\ \text{molecular sieves}}]{PdBr_2,\ NaOH,\ CH_2Cl_2} Ph_2CO_3 + H_2O \quad (1)$$

$$PhBr + PhSH/30\%\ NaOH \xrightarrow[Ph_3P,\ PhCH_3]{Ph(PPh_3)_2PdBr} PhSPh \quad (2)$$

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[1] E.W.R. Steacie Fellow, 1980–1982.

[2] Hallgren, J. E.; Lucas, G. M. *J. Organomet. Chem.* **1981**, *212*, 135.

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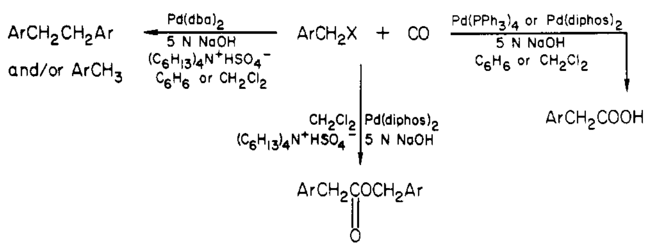
Scheme I



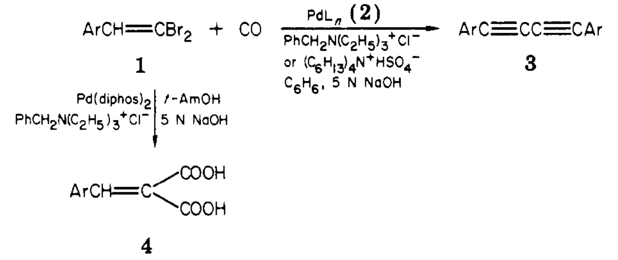
and arylation reactions,[6,7] catalyzed by palladium chloride under acidic conditions, have also been reported in the literature.

Recently, it has been demonstrated that ligands have a significant influence on the course of the palladium(0)-catalyzed and phase transfer catalyzed carbonylations of benzylic halides.[8] When the latter was carbonylated, under biphasic conditions (5 N NaOH, CH_2Cl_2), in the presence of tetrakis(triphenylphosphine)palladium(0), carboxylic acids were formed (Scheme I). As in the sulfide synthesis (eq 2) the use of a phase-transfer catalyst in the synthesis of carboxylic acids is not mandatory. Acids were also obtained when $Pd(diphos)_2$ (diphos = 1,2-bis(diphenylphosphino)ethane) was used as the metal catalyst under two-phase conditions, while the presence of a phase-transfer agent afforded esters. The use of bis(dibenzylideneacetone)palladium(0), which bears an acceptor ligand, for the phase transfer catalyzed reaction results in coupling and/or dehalogenation. No reaction occurs in the absence of a quarternary ammonium salt.

To our knowledge, the metal complex catalyzed carbonylation of vinylic dibromides has not been investigated. We anticipated that such dibromides, readily prepared by treatment of carbonyl compounds with carbon tetrabromide and triphenylphosphine, could be carbonylated to unsaturated dicarboxylic acids. We now wish to report that vinylic dibromides undergo several selective and useful reactions, subject to the nature of the organic substrate, but that ligands have little influence on these particular phase-transfer processes.

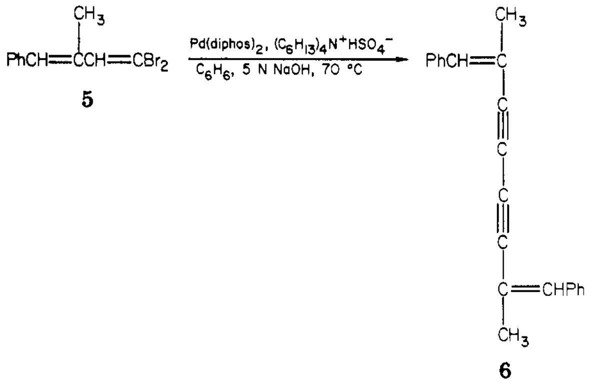
Results and Discussion

Treatment of β,β-dibromostyrene (**1**, Ar = Ph) with carbon monoxide, tetrakis(triphenylphosphine)palladium(0) (**2**, L = PPh_3, n = 4) as the metal catalyst (50:1 ratio of **1**/**2**), and benzyltriethylammonium chloride or tetrahexylammonium hydrogen sulfate as the phase-transfer agent, in a two-phase system (C_6H_6, 5 N NaOH) at 55 °C afforded 1,4-diphenyl-1,3-butadiyne (**3**, Ar = Ph) in 40% yield. The yield of **3**, Ar = Ph, increased to 54% by using $Ph(diphos)_2$ (**2**, L = $Ph_2PCH_2CH_2PPh_2$, n = 2) as the metal-containing catalyst. Reasonable yields (56–74%) of diynes (**3**, Ar = p = $CH_3C_6H_4$, p-ClC_6H_4) were realized by the use of other vinylic dibromides (derived from aromatic aldehydes) as substrates and a palladium catalyst. Substitution of methylene chloride for benzene as the organic phase resulted in higher (**1**, Ar = p-$CH_3C_6H_4$, $Pd(PPh_3)_4$) or lower (**1**, Ar = 4-$CH_3OC_6H_4$, $Pd(PPh_3)_4$) yields. No reaction occurred when the phase-transfer process was carried out in the absence of palladium catalyst. Also, no diyne was obtained (91% starting material was recovered) when **1**, Ar = p-$CH_3OC_6H_4$, was treated with carbon monoxide and a catalytic amount of **2**, L = PPh_3, n = 4, in tetrahydrofuran (60 °C, 4 h)—i.e., a one-phase reaction. The reaction time and temperature, catalyst, organic phase, and product yields for the phase-transfer reactions are listed in Table I.

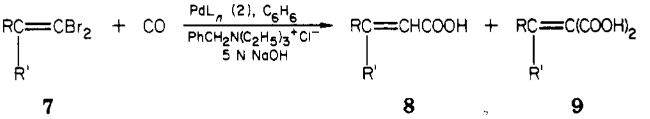


It is noteworthy that while the use of different palladium catalysts, i.e., $Pd(PPh_3)_4$, $Pd(diphos)_2$, and $Pd(dba)_2$ (dba = dibenzylideneacetone) results in changes in product yields, the reaction course is the same in all instances. These findings contrast with those obtained with benzylic bromide.[8]

The coupling reaction is not only applicable to **1** but also to the dibromide **5** obtained from α-methylcinnamaldehyde. Treatment of **5** under the conditions described for **1** afforded the polyunsaturated hydrocarbon **6** in 41% yield.



While catalyst ligands have little influence on the phase-transfer reactions of vinylic dibromides, the nature of the substrate and solvent significantly affects the reaction course. Carbonylation, rather than coupling, occurs when a dibromide **7**, R = alkyl, R′ = H, prepared from an aliphatic aldehyde, is reacted under the usual phase-transfer conditions, with benzene as the organic phase. The monoacid **8** is the major or only product obtained when **7**, R = cyclohexyl, n-C_6H_{13}, R′ = H, was used as the reactant, with diacid **9** formed as a byproduct. Diyne formation was not detected in these reactions. Similarly, dibromides derived from the cyclic ketones 4-*tert*-butylcyclohexanone and 4-methylcyclohexanone also gave **8** as the major or only product. In the latter reactions, diynes of course could not be formed.



When the polar solvent *tert*-amyl alcohol was employed as the organic phase in these phase-transfer reactions, double carbonylation occurs to give the diacids **4** or **9** in 28–93% yields. Benzyltriethylammonium chloride is a better phase-transfer catalyst for this reaction than tet-

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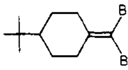
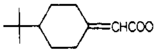
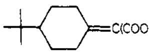
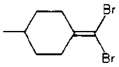
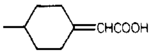
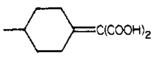
Table I. Phase Transfer Catalyzed Carbonylation Reactions of Vinylic Dibromides with Palladium(0) Catalysts

dibromide	cat. 2, L =	organic phase	oil bath temp, °C	reactn time, h	product[a]	yield,[b] %
1, Ar = Ph	PPh_3	C_6H_6	55	42	3, Ar = Ph	40
	diphos	C_6H_6	70	70	3, Ar = Ph	54
	diphos	*t*-AmOH	50	19	4, Ar = Ph	93
1, Ar = *p*-$CH_3C_6H_4$	PPh_3	C_6H_6	50	42	3, Ar = *p*-$CH_3C_6H_4$	36
	PPh_3	CH_2Cl_2	50	41	3, Ar = *p*-$CH_3C_6H_4$	43
	dba	C_6H_6	50	48	3, Ar = *p*-$CH_3C_6H_4$	42
	diphos	C_6H_6	40	42	3, Ar = *p*-$CH_3C_6H_4$	56
1, Ar = *p*-$CH_3OC_6H_4$	PPh_3	C_6H_6	70	41	3, Ar = *p*-$CH_3OC_6H_4$	49
	PPh_3	CH_2Cl_2	50	43	3, Ar = *p*-$CH_3OC_6H_4$	20
	diphos	C_6H_6	70	45	3, Ar = *p*-$CH_3OC_6H_4$	61
	diphos	*t*-AmOH	50	22	4, Ar = *p*-$CH_3OC_6H_4$	87
1, Ar = *p*-ClC_6H_4	diphos	C_6H_6	70	48	3, Ar = *p*-ClC_6H_4	74
5	diphos	C_6H_6	70	68	6	41
 (7)	diphos	C_6H_6	75	29	 (8)	84
	diphos	*t*-AmOH	50	29	 (9)	80
 (7)	diphos	C_6H_6	70	22	 (8 + 9)[c]	33
	diphos	*t*-AmOH	50	40	 (9)	28
7, R = *n*-C_6H_{13}, R′ = H	diphos	C_6H_6	70	70	8, R = *n*-C_6H_{13}, R′ = H	55
7, R = cyclohexyl, R′ = H	diphos	C_6H_6	70	43	8, R = cyclohexyl, R′ = H	6
	diphos	*t*-AmOH	50	42	9, R = cyclohexyl, R′ = H	32
7, R = $C_2H_5CHCH_3$, R′ = H	diphos	C_6H_6	70	40	8, R = $C_2H_5CHCH_3$, R′ = H	64
	diphos	*t*-AmOH	50	42	9, R = $C_2H_5CHCH_3$, R′ = H[d]	82
7, R = R′ = Ph	diphos	*t*-AmOH	50	20	8 and 9, R = R′ = Ph[e]	59

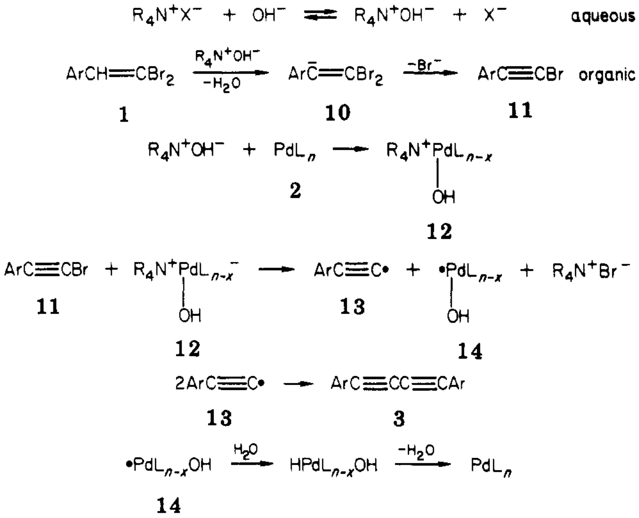
[a] Products were identified on the basis of analytical and spectral data. Pertinent spectral data for new compounds are given in the Experimental Section. [b] Yields are of pure materials. [c] Ratio of 8/9 was 3.5:1.0. [d] Less than 3% of 18, R = $C_2H_5CH(CH_3)$, R′ = H, was also isolated. [e] Ratio of 8/9 was 1:6.

rahexylammonium hydrogen sulfate. This reaction is not only applicable to aliphatic and cycloalkyl vinylic dibromides but also to dibromides derived from aromatic aldehydes. For example, carbonylation of *β*,*β*-dibromostyrene (1, Ar = Ph) under these conditions ($Pd(diphos)_2$ and $PhCH_2N(C_2H_5)_3{}^+Cl^-$ as catalysts) afforded benzylidenemalonic acid (4, Ar = Ph) in 93% yield. A mixture of benzylidenemalonic and cinnamic acids were formed in a total yield of 30% when the latter reaction was effected in the absence of the phase-transfer agent.

Only in the case of 7, R = R′ = Ph (i.e., from benzophenone), was monoacid produced together with diacid in the phase-transfer reactions with *tert*-amyl alcohol as the organic phase. Starting material was recovered when the carbonylation reaction of 7, R = R′ = Ph, was repeated by using benzene as the organic solvent.

Let us now consider the possible mechanisms for the three different reactions described above. First, the formation of diynes can be rationalized by the pathway outlined in Scheme II. The presence of an aromatic substituent in the dibromide renders the vinylic dibromide sufficiently acidic so that it can be deprotonated by the quarternary ammonium hydroxide (generated in the aqueous phase by displacement of the phase-transfer agent and then transferred to the organic phase), giving the carbanion 10. Elimination of the bromide ion from the latter would give the bromoarylalkyne 11. In addition to the deprotonation of 1, the quaternary ammonium hydroxide can displace a phosphine ligand of the catalyst to give 12. Subsequent electron-transfer reaction of 12 with bromoarylalkyne 11 would give the alkynyl radical 13, together with 14 and a quaternary ammonium halide (which can be transferred to the aqueous phase). The diyne 3 could then arise by radical dimerization of 13. The palladium catalyst may, perhaps, be regenerated by hydrogen abstraction by 14 at the interface followed by dehydration.

Scheme II



$$R_4N^+X^- + OH^- \rightleftharpoons R_4N^+OH^- + X^- \quad \text{aqueous}$$

$$\underset{1}{ArCH{=}CBr_2} \xrightarrow[-H_2O]{R_4N^+OH^-} \underset{10}{Ar\bar{C}{=}CBr_2} \xrightarrow{-Br^-} \underset{11}{ArC{\equiv}CBr} \quad \text{organic}$$

$$R_4N^+OH^- + \underset{2}{PdL_n} \longrightarrow \underset{12}{R_4N^+\underset{OH}{\underset{|}{Pd}}L_{n-x}}$$

$$\underset{11}{ArC{\equiv}CBr} + \underset{12}{R_4N^+\underset{OH}{\underset{|}{Pd}}L_{n-x}^-} \longrightarrow \underset{13}{ArC{\equiv}C\bullet} + \underset{14}{\bullet\underset{OH}{\underset{|}{Pd}}L_{n-x}} + R_4N^+Br^-$$

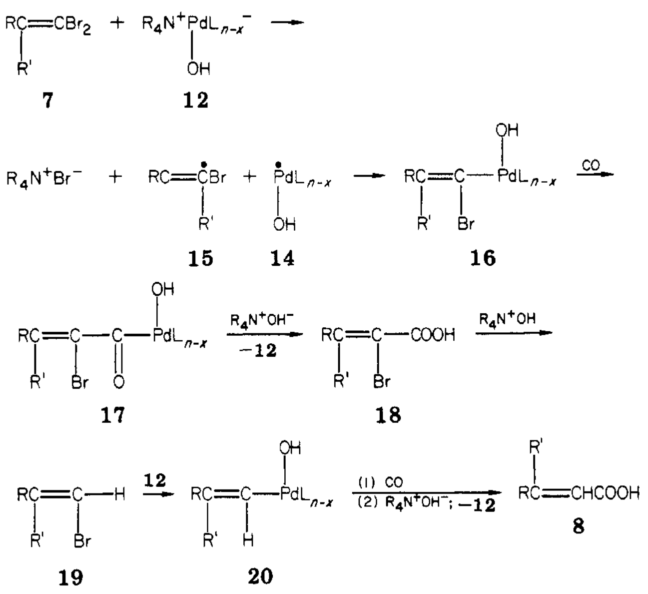
$$\underset{13}{2ArC{\equiv}C\bullet} \longrightarrow \underset{3}{ArC{\equiv}CC{\equiv}CAr}$$

$$\underset{14}{\bullet PdL_{n-x}OH} \xrightarrow{H_2O} HPdL_{n-x}OH \xrightarrow{-H_2O} PdL_n$$

$x = 1$ for PPh_3; $x = 0.5$ for dba, diphos

Good evidence for the intermediacy of 11 was obtained by using bromophenylacetylene (11, Ar = Ph) as the substrate. Treatment of bromophenylacetylene under conditions identical with that described for 1, Ar = Ph ($Pd(diphos)_2$, $PhCH_2N(C_2H_5)_3Cl$, 5 N NaOH, C_6H_6) except

Scheme III



that a shorter reaction time (18 h at 70 °C) was used, gave the diyne 3, Ar = Ph, in 38% yield (the yield of 3, Ar = Ph, from 1, R = Ph, was 54%; however, that was after 70 h at 70 °C). No diyne was obtained when 11, Ar = Ph, was reacted in the absence of the phase-transfer catalyst. The hydroxide ion displacement of a phosphine ligand of the palladium catalyst 2 has been previously proposed,[8] and the crown ether catalyzed displacement of a neutral phosphine ligand of a mononuclear platinum complex by an anionic ligand (cyanide ion) has been reported by Fakley and Pidcock.[9] While an ionic pathway cannot be rule out in the reaction of 11 with 12, support has recently been obtained for the participation of radicals in the coupling and reduction reaction of benzylic halides with bis(dibenzylideneacetone)palladium under phase-transfer conditions.[8]

The vinylic proton of an unsaturated dibromide, derived from an aliphatic aldehyde (7, R = alkyl, R′ = H), is much less acidic than the corresponding proton of 1. Consequently, deprotonation of 7, R = alkyl, R′ = H, by the quaternary ammonium hydroxide does not occur. Rather, carbonylation of 7, R = alkyl, R′ = H, with benzene as the organic phase gives the monoacid as the main or only product. Vinylic dibromides derived from 4-methyl- and 4-*tert*-butylcyclohexanone undergo similar transformations. The monoacid does *not* arise by decarboxylation of the diacid since exposure of 9, R = R′ = $(CH_2)_2CH(t\text{-}Bu)(CH_2)_2$, to CO/5 N NaOH/$PhCH_2N(C_2H_5)_3{}^+Cl^-/C_6H_6$ at 70 °C for 24 h, in either the absence or presence of $Pd(diphos)_2$, only resulted in the recovery of the diacid 9.

A pathway for the formation of monoacids from vinylic dibromides is given in Scheme III. Single electron-transfer reaction of 7 with 12 would give the radicals 15 and 14, together with bromide ion. Coupling of the two radicals would then afford the vinylpalladium complex 16. An alternative route to 16 (except that the hydroxyl ligand would be replaced by bromide) can involve oxidative addition of PdL_n to the vinylic dibromide. Carbonylation of 16 (to 17) and base-induced acyl carbon–palladium bond cleavage would give the unsaturated bromoacid 18 and regenerate 12. Decarboxylation of 18, under the basic conditions, would give the vinylic bromide 19. The conversion of 19 to 8 (i.e., via 20) can then occur by the same pathway as that for the formation of the bromoacid 18 from the dibromide 7. Phase-transfer carbonylation of the monobromide 2-bromo-2-butene under the above conditions does indeed give the monocarboxylic acid. If the pathway in Scheme III is valid, then the acid function of the product 8 is not the same as the carboxyl function in the intermediate bromoacid 18.

The conversion of *all* types of vinylic dibromides to diacids 4 and 9 when *tert*-amyl alcohol was used as the organic phase may be due to solvation effects. For example, when the bromoacid 18 is generated in *tert*-amyl alcohol, it can be solvated by hydrogen bonding to the organic phase (unlike benzene). This solvation effect may retard the decarboxylation of 18 and permit the carbonylation of the vinylic bromide functionality to give the diacid (by a scheme analogous to the conversion of 7 to 18 or 19 to 8). The failure to observe the formation of diynes in the case of vinylic dibromide derived from aromatic aldehydes (i.e., 1), using *tert*-amyl alcohol as the organic phase, may be due to solvation of hydroxide ion or the dibromide, either process inhibiting the dehydrobromination of 1 to give the bromoarylalkyne.

It should also be noted that a small quantity (<3%) of the bromoacid byproduct 18, R = $C_2H_5CH(CH_3)$, R′ = H, was isolated from the double carbonylation of 7, R = $C_2H_5CH(CH_3)$, R′ = H, by using *tert*-amyl alcohol as the organic phase.

In conclusion, vinylic dibromides can be converted to diynes, monoacids, and diacids by palladium(0)-catalyzed and phase-transfer catalyzed carbonylation reactions. These highly or completely selective reactions are sensitive to the nature of the organic substrate, and to the organic phase. The diacid synthesis constitutes a two-step method for the preparation of such molecules from a wide variety of aldehydes and ketones. Solid evidence has been obtained for several of the intermediates in these phase-transfer reactions.

Experimental Section

Analytical determination were carried out by Canadian Microanalytical Service, Vancouver, Canada. Mass spectra were recorded on a VG 7070E spectrometer. Infrared spectral determinations were made with a Unicam SP-1100 spectrometer, equipped with a calibration standard. Proton magnetic resonance spectra were recorded on a Varian T60 or EM360 spectrometer, and carbon magnetic resonance spectral determinations were made in the fully and partially decoupled modes with a Varian FT-80 spectrometer.

Tetrakis(triphenylphosphine)palladium(0) was prepared according to the procedure of Coulson.[11] Literature procedures were also used to synthesize $Pd(dba)_2$[12] and $Pd(diphos)_2$.[13] Occasionally, commercial catalysts were used, but yields were slightly lower than with freshly synthesized materials. Solvents were purified by standard methods.

1,1-Dibromo Olefins. Vinylic dibromides, derived from aldehydes, were prepared by using carbon tetrabromide and triphenylphosphine.[14] The required compounds were purified by column chromatography (silica or alumina) with hexane as the eluant, reduced pressure distillation, or in the case of 5 by high-pressure liquid chromatography (90:1 hexane/ethyl acetate). The procedure of Posner and co-workers[15] was used to convert

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Table II. Analytical Data for New Compounds

compd	molecular formula	C calcd	C found	H calcd	H found
6	$C_{22}H_{18}$	93.57	93.52	6.43	6.66
9, R = R′ = $(CH_2)_2CH(t\text{-}Bu)(CH_2)_2$	$C_{13}H_{20}O_4$	64.98	65.11	8.39	8.02
9, R = R′ = $(CH_2)_2CH(CH_3)(CH_2)_2$	$C_{10}H_{14}O_4$	60.59	60.92	7.12	7.14
9, R = C_6H_{11}, R′ = H	$C_{10}H_{14}O_4$	60.59	60.71	7.12	6.83
9, R = $C_2H_5CH(CH_3)$, R′ = H	$C_8H_{12}O_4$	55.80	56.08	7.02	7.26

ketones to 1,1-dibromo olefins, except for $Ph_2C{=}CBr_2$ which was prepared by the method of Kobrich et al.[16] The following vinylic dibromides are new.

1, Ar = p-$CH_3C_6H_4$: IR (neat) $\nu_{C=C}$ 1612 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (s, 3 H, CH_3), 7.10 (d, 2 H, aromatic, J = 8 Hz), 7.37 (s, 1 H, CH=), 7.40 (d, 2 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.36 (q), 88.54 (s), 128.28 (d), 129.05 (d), 132.39 (s), 136.73 (d), 138.54 (s).

1, Ar = p-ClC_6H_4: IR (neat) $\nu_{C=C}$ 1596 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.19 (d, 2 H, aromatic, J = 9 Hz), 7.30 (s, 1 H, CH=), 7.38 (d, 2 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 90.46 (s), 128.64 (d), 129.62 (d), 133.67 (s), 134.35 (s), 135.62 (d).

5: IR (neat) $\nu_{C=C}$ 1625, 1599 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10 (s, 3 H, CH_3), 6.67 (br s, 1 H, Ph*CH*=), 7.07 (s, 1 H, *CH*=CBr_2), 7.23 (s, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 17.14 (q), 87.56 (s), 127.20 (d), 128.23 (d), 129.08 (d), 133.40 (s), 133.89 (d), 136.66 (s), 141.10 (d).

7, R = R′ = $(CH_2)_2CH(t\text{-}Bu)(CH_2)_2$: ^1H NMR ($CDCl_3$) δ 0.87 (s, 9 H, t-Bu), 1.03–2.33, 2.87, (m, 9 H, aliphatic protons); ^{13}C NMR ($CDCl_3$) δ 27.52 (q), 27.54 (d), 32.31 (s), 34.61 (t), 47.45 (t), 81.48 (s), 144.90 (s).

7, R = R′ = $(CH_2)_2CH(CH_3)(CH_2)_2$: ^1H NMR ($CDCl_3$) δ 1.10 (d, 3 H, CH_3), 0.90–2.20 (m, 5 H, ring protons), 2.80, 3.00 (m, 4 H, allylic protons).

7, R = cyclohexyl, R′ = H: IR (neat) $\nu_{C=C}$ 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–2.00 (m, 10 H, CH_2), 2.20 (m, 1 H, CH of ring), 6.20 (d, 1 H, J = 9 Hz, olefinic proton).

7, R = $C_2H_5CH(CH_3)$, R′ = H: IR (neat) $\nu_{C=C}$ 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85–1.30 (m, 8 H, C_2H_5, CH_3), 2.40 (m, 1 H, saturated CH), 6.10 (d, 1 H, J = 9 Hz, CH=).

General Procedure for the Palladium(0)-Catalyzed Reaction of Vinylic Dibromides with Carbon Monoxide under Phase-Transfer Conditions. Benzyltriethylammonium chloride or tetra-n-hexylammonium hydrogen sulfate (0.20–0.40 mmol) was dissolved in 15 mL of 5 N NaOH under a nitrogen atmosphere. The gas was changed to carbon monoxide, and the palladium(0) catalyst (0.08–0.10 mmol) in benzene or *tert*-amyl alcohol (15 mL) was added dropwise to the 5 N NaOH solution. When (Pd(diphos)$_2$ was used as the catalyst, it was first dissolved in 1 mL of methylene chloride, diluted with benzene or *tert*-amyl alcohol (15 mL), and then added to 5 N NaOH. The reaction mixture was vigorously stirred for 4 h at room temperature. The vinylic dibromide, dissolved in 2–4 mL of benzene or *tert*-amyl alcohol, was added drop-by-drop over a period of 1 h. The reaction mixture was heated with stirring until the reactant dibromide was consumed (see Table I for reaction times and temperatures). The layers were separated, and the aqueous phase was treated with ether, and the ether portion was then combined with the organic phase. The combined organic phase was dried ($MgSO_4$), concentrated, and then chromatographed on silica gel or alumina to give the pure product.

The aqueous layer was neutralized with dilute hydrochloric acid (5 N) and then extracted with ether (3 × 50 mL). The ether extract was dried ($MgSO_4$) and concentrated to yield the product.

All of the known compounds were identified by comparison of physical data (mp or bp, IR, NMR, MS), with those for authentic materials. The following compounds are new (see Table II for analytical data).

6: mp 79–80 °C; IR ($CHCl_3$) $\nu_{C=C}$ 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10 (s, 6 H, CH_3), 6.97 (s, 2 H, olefinic protons), 7.30 (s, 10 H, Ph); MS, m/e 282 [M]$^+$.

9, R = R′ = $(CH_2)_2CH(t\text{-}Bu)(CH_2)_2$: mp 178 °C dec; IR ($CHCl_3$) ν_{CO} 1700 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 0.86 (s, 9 H, t-Bu), 1.00–2.40 (m, 9 H, ring protons), 9.8 (br s, 2 H, COOH); MS (bis(trimethylsilyl)derivative), m/e 384 [M]$^+$.

9, R = R′ = $(CH_2)_2CH(CH_3)(CH_2)_2$: IR ($CHCl_3$) ν_{CO} 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00–2.80 (m, 12 H, protons on saturated carbons), 9.50 (br s, 2 H, COOH).

9, R = cyclohexyl, R′ = H: oil; IR (neat) ν_{CO} 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–3.00 (m, 11 H, C_6H_{11}), 7.40 (d, 1 H, CH=), 10.90 (s, 2 H, acid protons); ^{13}C NMR ($CDCl_3$) δ 168.0, 169.7 (carbonyl carbons); MS (bis(trimethylsilyl)derivative), m/e 342 [M]$^+$.

9, R = $C_2H_5CHCH_3$, R′ = H: Ir (neat) ν_{CO} 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80–2.40 (m, 8 H, methyl and methylene protons), 3.00 (m, 1 H, saturated methine proton), 7.42 (d, 1 H, CH=), 9.60 (s, 2 H, COOH); MS (bis(trimethylsilyl)derivative), m/e 316 [M]$^+$.

Pd(diphos)$_2$-Catalyzed Reaction of Bromophenylacetylene (11, Ar = Ph). The general procedure, described for vinylic dibromides, was applied to bromophenylacetylene[17] (i.e., Pd[diphos]$_2$, $PhCH_2N(C_2H_5)_3Cl$, 5 N NaOH, C_6H_6). After 18 h at 70 °C and subsequent workup, **3**, Ar = Ph, was isolated in 38% yield.

The starting material **11** was recovered when the reaction was run in the absence of benzyltriethylammonium chloride.

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Registry No. **1** (Ar = Ph), 7436-90-0; **1** (Ar = p-$CH_3C_6H_4$), 60512-56-3; **1** (Ar = p-$CH_3OC_6H_4$), 60512-57-4; **1** (Ar = p-ClC_6H_4), 77295-59-1; **2** (L = PPh_3, n = 4), 14221-01-3; **2** (L = diphos, n = 2), 31277-98-2; **2** (L = dbq, n = 2), 32005-36-0; **3** (Ar = Ph), 886-66-8; **3** (Ar = p-$CH_3C_6H_4$), 22666-07-5; **3** (Ar = p-$CH_3OC_6H_4$), 22779-05-1; **3** (Ar = p-ClC_6H_4), 51118-06-0; **4** (Ar = Ph), 584-45-2; **4** (Ar = p-$CH_3OC_6H_4$), 21405-61-8; **5**, 77295-77-3; **6**, 85066-82-6; **7** (R = R′ = $(CH_2)_2CH(Bu\text{-}t)(CH_2)_2$), 56881-81-3; **7** (R = R′ = $(CH_2)_2CH(CH_3)(CH_2)_2$), 64285-83-2; **7** (R = n-C_6H_{13}, R′ = H), 73383-25-2; **7** (R = cyyclohexyl, R′ = H), 60754-49-6; **7** (R = $C_2H_5CH(CH_3)$, R′ = H), 85066-83-7; **7** (R = R′ = Ph), 2592-73-6; **8** (R = R′ = $(CH_2)_2CH(Bu\text{-}t)(CH_2)_2$), 13733-51-2; **8** (R = R′ = $(CH_2)_2CH(CH_3)(CH_2)_2$), 56300-86-8; **8** (R = n-C_6H_{13}, R′ = H), 3760-11-0; **8** (R = cyclohexyl, R′ = H), 4484-35-9; **8** (R = $C_2H_5CH(CH_3)$, R′ = H), 37549-83-0; **8** (R = R′ = Ph), 606-84-8; **9** (R = R′ = $(CH_2)_2CH(Bu\text{-}t)(CH_2)_2$), 85066-84-8; **9** (R = R′ = $(CH_2)_2CH(CH_3)(CH_2)_2$), 85066-85-9; **9** (R = cyclohexyl, R′ = H), 85066-86-0; **9** (R = $C_2H_5CH(CH_3)$, R′ = H), 85066-87-1; **9** (R = R′ = Ph), 4472-94-0.

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