acetone, and the extract was evaporated under vacuum. The oily residue was taken up in 300 ml of methanol containing 0.5 ml of concentrated sulfuric acid. This solution was refluxed for 12 h, then diluted with water and extracted thoroughly with methylene chloride. The extract was concentrated under vacuum, and the residue stirred for 10 min with 50 ml of 5% hydrochloric acid. Standard workup (methylene chloride) gave 11g of crude keto ester **17**, whose quality was improved by quick passage of the material in ether through a small column of silica gel. The keto ester (10 g) showed a major ir absorption at 1740 cm^{-1}; ^{1}H NMR δ 3.67 (6 H), 2.2–2.4 (8 H), 1.8–2.1 (4 H), and 1.4–1.6 ppm (2 H).

A solution of **17** in 400 ml of dry tetrahydrofuran under nitrogen was mixed with 17 g of potassium *tert*-butoxide at room temperature. The suspension was stirred for 26 h. The mixture was quenched in an equal volume of saturated, aqueous potassium dihydrogen phosphate solution. Standard workup (methylene chloride) gave a solid residue which was purified by chromatography on silica gel using ether followed by 4:1 ether/acetone as eluent. Crystallization from methanol of the residue from evaporation of the ether/acetone eluate gave 1.5 g (6% overall) of pure triketone: mp 120–121 °C; ir ν 1776, 1742, and 1718 cm^{-1}; ^{1}H NMR δ 3.2–3.5 (4 H), 2.2–2.5 (6 H), and 1.6–1.8 ppm (2 H); ^{13}C NMR δ 208.4, 199.1 (approximate ratio 2:1), and 63.3, 40.8, 38.5, and 22.4 ppm (each of approximately equal intensity).

Acknowledgment. We are grateful to the National Institutes of Health (CA-12,961) and the National Science Foundation (GP-30568X) for financial support and to John Ivy for assistance. Funds for the purchase of the NMR instruments essential to this work were provided, in part, by the National Cancer Institute (CA-14599) via The University of Chicago Cancer Research Center, and by the National Science Foundation. C.G. thanks Montedison S.p.A., Centro Ricerche di Chimica Organica, for a leave of absence.

Registry No.—**3**, 58866-18-5; **3** 2,4-DNP, 58866-19-6; **4**, 58866-20-9; **5**, 17610-48-9; **6**, 58866-21-0; **7**, 58866-22-1; **8**, 58866-23-2; **8** 2,4-DNP, 58866-24-3; **9**, 25886-63-9; **10**, 41065-49-0; **11**, 58866-25-4; **12**, 58866-26-5; **13**, 58866-27-6; **14**, 58866-28-7; **17**, 58866-29-8; cyclopentyllithium, 23473-12-3; cyclopentylnitrile, 4254-02-8.

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Mercury in Organic Chemistry. 7.[1] A Convenient Synthesis of Symmetrical Conjugated Dienes and Polyenes

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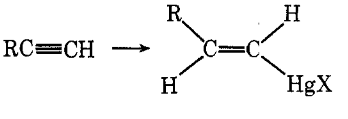
Received December 18, 1975

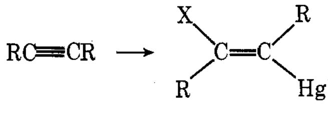
Vinylmercuric chlorides undergo reaction with palladium chloride and lithium chloride in hexamethylphosphoramide at 0 °C to provide essentially quantitative yields of the corresponding symmetrical conjugated dienes. This reaction is especially valuable for the synthesis of functionally substituted dienes and symmetrical polyenes. Divinylpalladium species are presumed to be intermediates in these reactions.

Conjugated dienes are of considerable importance in organic chemistry in themselves,[2] as well as for their utilization in the Diels–Alder reaction. Recently a number of new methods for the preparation of conjugated dienes have appeared utilizing organoaluminum,[3] -boron,[3b,4] -cobalt,[5] -copper,[6] -lithium,[5,6a–d,f,7] -magnesium,[6e] -nickel,[8] and -silver[6b,7] reagents. The scope of many of these reactions is limited by the nature of the organometallic involved or the procedure employed. Very few functional groups have been incorporated in these reactions. We wish to report a convenient new stereospecific coupling procedure utilizing vinylmercurials which both tolerates functionality and produces symmetrical dienes in near-quantitative yield. Furthermore, the reaction appears widely applicable to the preparation of symmetrical polyenes.

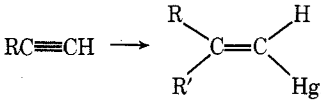
We previously reported convenient procedures for the stereospecific conversion of acetylenes into vinylmercuric halides in high yields (eq 1).[9] Other vinylmercurials are now available through the mercuration of acetylenes (eq 2, 3).[10,11]



$$\mathrm{RC{\equiv}CH} \longrightarrow \overset{\mathrm{R}}{\underset{\mathrm{H}}{}}\mathrm{C{=}C}\overset{\mathrm{H}}{\underset{\mathrm{HgX}}{}} \qquad (1)$$



$$\mathrm{RC{\equiv}CR} \longrightarrow \overset{\mathrm{X}}{\underset{\mathrm{R}}{}}\mathrm{C{=}C}\overset{\mathrm{R}}{\underset{\mathrm{HgX}}{}} \qquad (2)^{10}$$

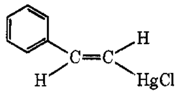
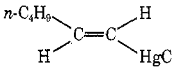
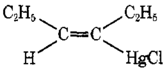


$$\mathrm{RC{\equiv}CH} \longrightarrow \overset{\mathrm{R}}{\underset{\mathrm{R'}}{}}\mathrm{C{=}C}\overset{\mathrm{H}}{\underset{\mathrm{HgX}}{}} \qquad (3)^{11}$$

Vinylmercurials possess a number of features making them attractive as synthetic intermediates. They are remarkably thermally and chemically stable organometallics. They are generally high melting, easily recrystallized solids, stable to air, water, bases, and dilute acids. These features allow one to run synthetic reactions employing these compounds under a wide variety of reaction conditions.

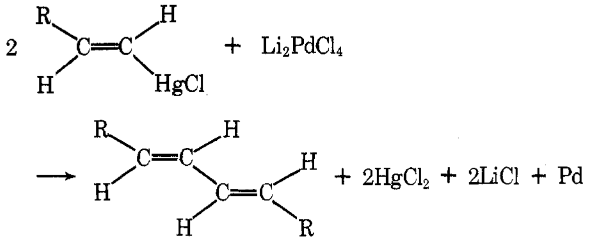
Recently vinylmercurials have proven valuable in the synthesis of α,β-unsaturated ketones,[12] acids,[1] and esters.[1] During the course of this latter study we observed that vinylmercuric chlorides when treated with palladium chloride and lithium chloride rapidly undergo dimerization to the

Table I. Reaction Conditions for Vinylmercuric Chloride Dimerization

Entry	Vinylmercuric chloride[a]	$PdCl_2$, mmol	LiCl, mmol	Solvent[b]	Temp, °C	Diene yield, %[c] trans, trans	cis, trans	cis, cis
1		1		HMPA	25	<5		
2			2			99		
3			4			100		
4		2				94	6	
5		1		C_6H_6		3		
6				Et_2O		4		
7				THF		29		
8				CH_3CN		50		
9				Pyridine		54		
10				Acetone		57		
11				CH_3OH		64		
12				DMF		82		
13				Me_2SO		82		
14				HMPA		68	15	
15					0	100		
16					25		5	75
17					0			75
18		2					7	33

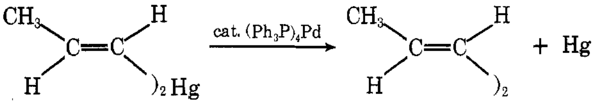
[a] 2 mmol. [b] 10 ml. [c] GLC analysis using an internal standard.

corresponding symmetrical conjugated dienes (eq 4). By the


(4)

proper choice of solvent and temperature we have been able to achieve an almost quantitative, highly stereospecific synthesis.

Near the completion of our work, Vedejs and Weeks reported a closely related dimerization of *cis*- and *trans*-dipropenylmercury using catalytic amounts of tetrakis(triphenylphosphine)palladium (eq 5).[13] While the catalytic as-


(5)

pect of this reaction is attractive, the increased volatility (and presumably toxicity) of liquid divinylmercurials over the high-melting solid vinylmercuric chlorides is a definite disadvantage. Furthermore, a 4–8% loss of stereospecificity was observed using the palladium(0) reagent. It was also reported that the use of palladium(II) reagents results in variable yields, low stereoselectivity, and in general a more complex reaction. Quite to the contrary, we have found conditions using palladium chloride under which the symmetrical dienes can be obtained in excellent yield and high stereospecificity.

Results and Discussion

Reaction Conditions. During the course of our earlier work on the palladium-promoted carbonylation of vinylmercurials,[1] we observed the appearance of minor amounts of conjugated dienes. In a subsequent effort to improve the yields of dienes obtained from this reaction, we have more carefully studied the effect of reagent, stoichiometry, solvent, and temperature. The results are reported in Table I.

A number of interesting observations can be drawn from the results. Styrylmercuric chloride reacts rapidly with palladium chloride with or without added lithium chloride, but only in its presence is the symmetrical diene obtained in good yield. Excess lithium chloride has no effect. On the other hand, excess palladium chloride decreases the stereospecificity of the reaction as well as the yield of diene (entries 4 and 18). The solvent also plays a critical role in these reactions. The yield of symmetrical diene increases steadily with the polarity of the solvent, hexamethylphosphoramide (HMPA) being the solvent of choice. Better yields and higher stereospecificity are also observed at lower temperatures.

Organophosphorus compounds often play a critical role in transition metal promoted reactions. In view of the importance of HMPA in the dimerization reaction, we chose to briefly examine the effect of other phosphorus compounds on the yield and stereochemistry of the reaction (Table II). No other phosphorus compound proved as effective as HMPA in promoting stereospecific dimerization. Even with only 4 equiv of HMPA in THF an excellent 95% yield of 1,4-diphenylbutadiene is obtained. Unfortunately, some loss of stereospecificity is observed. With tributyl phosphite a new reaction apparently ensues as metallic mercury, not mercuric chloride, is produced in high yield.

Synthesis of Dienes and Polyenes. The generality of the diene synthesis has been examined on a wide variety of vinylmercuric chlorides (Table III). Twenty millimoles of organomercurial was added to 10 mmol of palladium chloride and 40 mmol of lithium chloride in HMPA (100 ml) at 0 °C under nitrogen. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. The product is obtained by simply extracting with pentane, drying, and removing the solvent. Trans-monosubstituted vinylmercuric chlorides give excellent yields. *cis*-Stilbenylmercuric chloride dimerizes in quantitative yield, but *cis*-3-hexenylmercuric chloride gives a significantly lower yield. We presume that this is due to the presence of a neighboring allylic hydrogen which might undergo β-hydride elimination. A slightly reduced yield (82%) is also observed with the *trans*-β-acetoxymercurial. This might be due to either β-hydride or β-acetoxy elimination reactions. This type of dimerization should prove highly useful for the preparation of functionally, highly substituted dienes

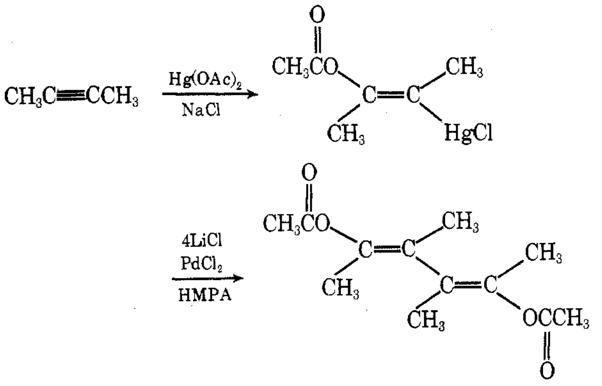
Table II. Effect of Phosphorus Compounds

$$2C_6H_5CH{=}CHHgCl + PdCl_2 \xrightarrow[THF]{0\ ^\circ C} (C_6H_5CH{=}CH)_2$$

Phosphorus compound[a]	Lithium chloride[b]	Diene yield, %[c] trans, trans	cis, trans	Total
Hexamethylphosphoramide	+	82	13	95
	–	0	0	0
Tributylphosphate	+	69	21	90
	–	~10	~5	~15
Tributylphosphine	+	45	2	47
	–	40	3	43
Triphenylphosphine[d]	–	36	22	58
Tributylphosphite	+	17	0	17[e]
	–	7	1	8[e]

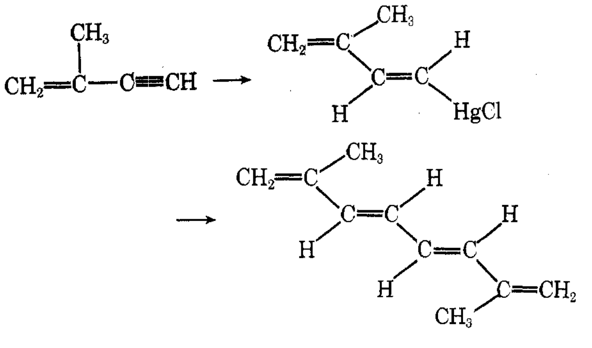
[a] 4 equiv per palladium chloride. [b] Either 4 equiv or none. [c] GLC analysis using a hydrocarbon internal standard. [d] Bis(triphenylphosphine)palladium chloride used. [e] Metallic mercury formed.

in view of the ready accessibility of such organomercurials (eq 6). The facile dimerization of two functionally substituted organomercurials in this study offers promise that this approach to dienes and polyenes might prove general for a wide variety of functionally substituted compounds. Both organomercury and -palladium compounds appear to tolerate a considerable range of functionality.



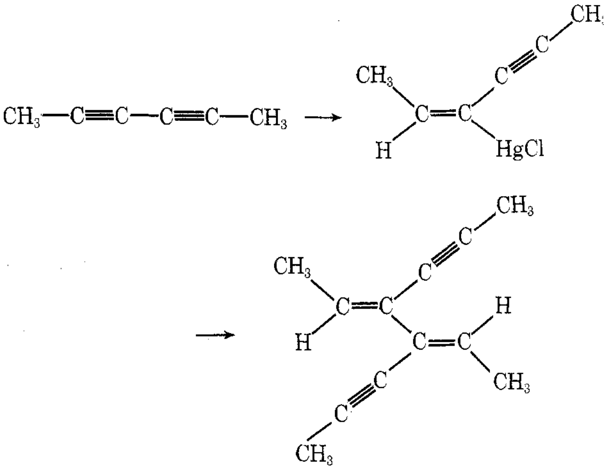
(6)

Especially noteworthy among the examples presented in Table III are the last two. Isopropenylacetylene can be selectively hydroborated on the triple bond by dicyclohexylborane. Mercuration gives a good yield of the corresponding dienylmercuric chloride.[9a] Dimerization and workup allow the preparation of the highly sensitive tetraene *trans,trans*-2,7-dimethyl-1,3,5,7-octatetraene in 95% yield (eq 7). All spectral data (NMR, uv, ir) are consistent with the assigned structure.



(7)

An equally interesting conversion is represented by the hydroboration–mercuration of 2,4-hexadiyne and subsequent dimerization of the resulting vinylmercuric chloride (eq 8). Hydroboration with disiamylborane produces the internally substituted vinylborane. The usual mercuration procedure[9a] gives a good yield of the acetylenic vinylmercuric chloride.



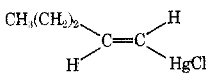
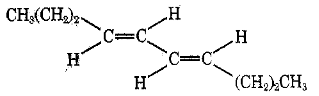
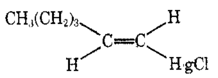
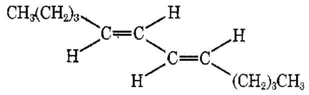
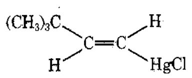
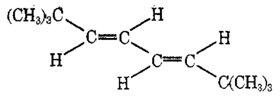
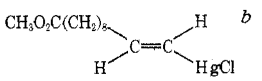
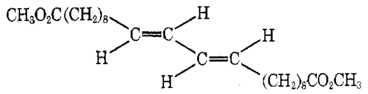
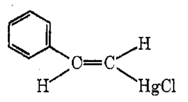
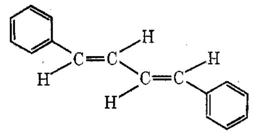
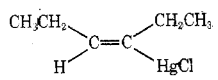
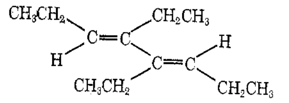
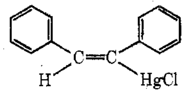
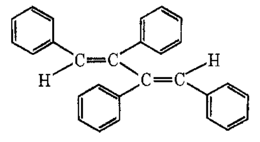
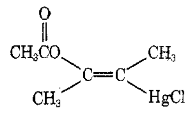
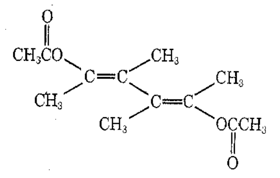
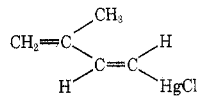
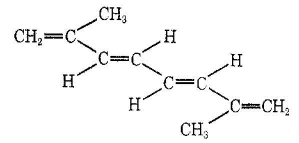
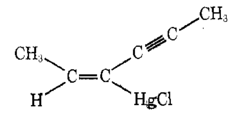
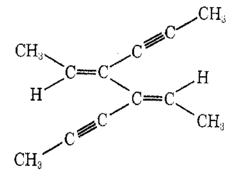
(8)

Dimerization provides a 92% yield of the pale yellow dienediyne readily recrystallized from pentane. Spectral data (NMR, ir, uv) are consistent with the assigned structure.

The above reactions appear to be highly stereospecific. All the simple 1,3-dienes whose yields were determined by gas chromatography were greater than 97% pure as determined by gas chromatographic comparison with authentic samples of all three possible stereoisomers. Crude *trans,trans*-2,2,7,7-tetramethyl-3,5-octadiene and (*Z,Z*)-1,2,3,4-tetraphenyl-1,3-butadiene gave NMR data consistent with the assigned structures and identical with the recrystallized compounds, which in turn had melting points identical with those of authentic samples prepared by alternate procedures. The stereochemistry of the *trans*-β-acetoxymercurial has been assigned from infrared data[14] and dimerization appears to give only one product as determined by NMR. *trans,trans*-2,7-Dimethyl-1,3,5,7-octatetraene exhibits a clean NMR spectra consistent with the assigned structure, as well as ir and uv data almost identical with those of *trans,trans*-1,3,5,7-octatetraene.[15] NMR examination of the dienediyne showed a very clean spectra consistent with the assigned structure and suggestive of only one product. Since hydroboration of 2,4-hexadiyne gives the cis vinylborane, the mercurial dimerization product is presumably (*E,E*)-4,5-diethylidene-2,6-octadiyne. The vinylmercurial derived from methyl 11-undecynoate was not obtained in isomerically pure form; so the resulting diene was a mixture.[1]

The accessibility of a variety of interesting functionally substituted vinylmercurials, the extreme ease with which dimerization occurs, and the ease with which dienes and polyenes can be isolated make this procedure particularly attractive for the synthesis of a number of otherwise difficultly accessible dienes and polyenes. This procedure should also

Table III. Synthesis of Dienes and Polyenes

Organomercurial	Registry no.	Dimer	Registry no.	Yield, %
	36525-00-5		53721-79-2	98[a]
	58873-33-9		30651-68-4	100[a]
	36525-02-7		22430-49-5	96
	56453-79-3		58873-35-1	94[b]
	36525-03-8		533-81-8	100[a]
	36525-04-9		30651-70-8	75[a]
	16188-35-5		1608-10-2	100
	16187-30-7		58873-36-2	82
	56453-81-7		58873-37-3	95
	58873-34-0		58873-38-4	92

[a] GLC analysis using an internal standard. [b] This organomercurial was not obtained in isomerically pure form via hydroboration–mercuration.

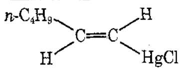
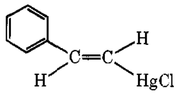
prove valuable for the synthesis of some of the naturally occurring symmetrical carotenoid polyenes.

Alkyl- and Arylmercurial Dimerization Reactions. The ease with which vinylmercurials undergo dimerization encouraged us to study the analogous reaction of alkyl- and arylmercurials. *n*-Hexylmercuric chloride reacts under our standard conditions as judged by a rapid color change from rust red to black. However, no dodecane was observed by GLC analysis. It is likely that palladium hydride elimination occurs to give a mixture of hexenes. To avoid this complication we have examined the dimerization of neopentyl-, allyl- and benzylmercuric halides. Neopentylmercuric chloride reacts only very slowly and no yield was determined. Allylmercuric iodide gave a ~70% yield of 1,5-hexadiene and benzylmercuric chloride dimerized to give a 56% yield of bibenzyl. This latter yield was improved to 70% by allowing the reaction to proceed for 10 days.

We have also examined the analogous coupling reactions of arylmercurials. Phenylmercuric chloride gave a rapid reaction and an 87% yield of biphenyl. However, perfluorophenylmercuric chloride reacts only very slowly and no yield was determined. Diphenylmercury gives a 95% yield of biphenyl based on utilization of both phenyl groups. These results are consistent with previous results on the dimerization of arylmercurials by palladium salts.[16]

Attempted Catalysis. Palladium catalysis of these dimerization reactions would substantially improve the synthetic utility of these reactions. We have previously achieved considerable success in using palladium chloride as a catalyst when cupric chloride is added as a reoxidant.[1] Unfortunately,

Table IV. Tetrakis(triphenylphosphine)palladium(0) Catalysis[a]

Vinylmercuric chloride[b]	Lithium chloride[c]	Diene yield, %[d] trans, trans	cis, trans	Total
	–	42	2	44
	+	59	2	61
	–	46	2	48
	+	80		80

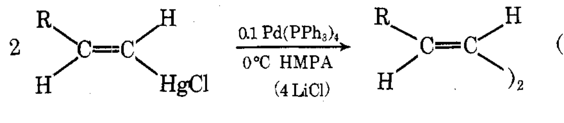
[a] 0.1 mmol catalyst. [b] 2.0 mmol. [c] Either 0 or 4 mmol. [d] GLC analysis using a hydrocarbon internal standard.

this approach failed in our present diene synthesis (eq 9).

$$2C_6H_5CH{=}CHHgCl + 2LiCl + 4CuCl_2 \xrightarrow[25\ ^\circ C,\ HMPA]{0.1\ PdCl_2} (C_6H_5CH{=}CH)_2 \quad (9)$$

$$15\%$$

Palladium(0) reagents should serve as catalysts without the need for additional reoxidants. Tetrakis(triphenylphosphine)palladium (10%), with and without added lithium chloride, has been added to both *trans*-1-hexenylmercuric chloride and styrylmercuric chloride in HMPA at 0 °C (eq 10).



(10)

$R = n\text{-}C_4H_9, C_6H_5$

An immediate darkening and deposition of metallic mercury occurs. Although the corresponding dienes are obtained in good yield when lithium chloride is present, the yields and stereospecificity are not as good as those of the stoichiometric palladium chloride reactions (Table IV).

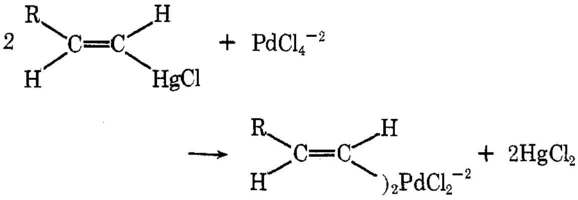
Mechanism. The direct coupling of aromatic compounds by palladium salts is a well-known reaction (eq 11).[16,17] Al-

$$2Ar{-}H + PdX_2 \longrightarrow Ar{-}Ar + Pd + 2HX \quad (11)$$

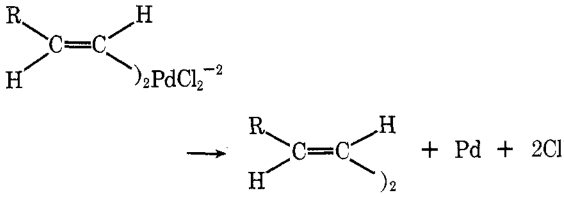
though intermediate arylpalladium compounds are undoubtedly involved, the precise manner by which coupling occurs is still unclear. Arylmercurials are also reportedly very readily coupled in the presence of palladium salts.[16] For example, Unger and Fouty report the rapid dimerization of tolylmercuric acetate in the presence of palladium acetate and perchloric acid. Bitolylmercury also rapidly couples when treated with "palladium salts" in acetic acid. Unfortunately, none of these experiments appear to have been done starting with the actual organomercurials indicated. Instead the mercurials were apparently prepared in situ and then treated with the palladium salts. Experimental details are lacking. In view of this previous report on arylmercurial dimerizations, it is not surprising that we also observe coupling products from both phenylmercuric chloride and diphenylmercury.

Vinylmercury or -palladium dimerization reactions have until recently been totally neglected. There are, however, several reports of the formation of dienes upon heating olefins and palladium acetate.[18-20] Vinylpalladium species may be involved in these reactions. Vedejs and Weeks have recently reported the smooth catalytic dimerization of *cis*- and *trans*-dipropenylmercury by tetrakis(triphenylphosphine)palladium.[13] Although they suggest no mechanism for this reaction, some of the side products observed clearly point to vinylpalladium intermediates.

Our palladium chloride–lithium chloride induced coupling of vinylmercuric chlorides also undoubtedly proceeds via intermediate vinylpalladium species. The facile carbonylation of these compounds by carbon monoxide is clear proof of their existence.[1] We suggest that these coupling reactions proceed through initial exchange to form a dichlorodivinylpalladium dianion (eq 12) which then reductively eliminates the diene, chloride anion, and palladium metal (eq 13). While palladium chloride also rapidly reacts with vinylmercurials, it presumably only forms a neutral divinylpalladium compound which apparently decomposes in a different manner. The chloride ligands presumably facilitate reductive elimination of the diene. The loss of stereospecificity and reduction in yield in the reaction employing excess palladium chloride most likely arises from formation of a monovinylpalladium anionic species which is no longer able to reductively eliminate the diene. Side reactions such as cis–trans isomerization then become increasingly important. The highly polar HMPA presumably promotes the formation of ionic species by solvation. It may also play a role in the stabilization of intermediate vinylpalladium species.



(12)



(13)

Conclusion

Vinylmercuric chlorides, readily available via acetylene addition reactions, undergo a rapid, stereospecific dimerization reaction with lithium chloride and palladium chloride in HMPA at 0 °C to provide excellent yields of the corresponding symmetrical 1,3-dienes. The reaction is applicable to the synthesis of functionally substituted dienes as well as polyenes. In attempting to extend these palladium-promoted reactions to the synthesis of unsymmetrical dienes we have recently uncovered a novel new route to π-allylpalladium compounds which we hope to report on shortly. Vinylmercury and -palladium reactions also provide a convenient new route to 1,4-dienes which we are presently studying.

Experimental Section

Reagents. All chemicals were used directly as obtained commercially unless indicated otherwise. Diethyl ether, THF, and HMPA were distilled from lithium aluminum hydride prior to use.

Phenylmercuric chloride (Aldrich) and diphenylmercury (Eastman Kodak) were used directly as obtained. Allylmercuric iodide,[21] benzylmercuric chloride,[22] *n*-hexylmercuric chloride,[23] neopentylmercuric chloride,[24] and *trans*-3-acetoxy-2-butenylmercuric chloride[14] were prepared according to literature procedures.

All other vinylmercuric chlorides were prepared using our standard hydroboration–mercuration sequence.[9] All vinylmercurials except that derived from 2,4-hexadiyne have been described before.[1,9] (*E*)-3-Chloromercuri-2-hexen-4-yne was prepared by hydroboration–mercuration of 2,4-hexadiyne using disiamylborane instead of dicyclohexylborane:[9a] mp 136–137 °C dec; ^1H NMR ($DCCl_3$) $\delta \sim 1.99$ (d, 3, $J = 7$ Hz, allyl), 2.01 (s, 3, propargyl) (overlapping peaks at 1.99 and 2.01), and 5.81 ppm (q, 1, $J = 7$ Hz, vinyl). Anal. Calcd for C_6H_7ClHg: C, 22.87; H, 2.24; Hg, 63.65. Found: C, 22.94; H, 2.32; Hg, 63.56.

Tetrakis(triphenylphosphine)palladium was prepared according to the literature procedure.[25] The palladium chloride was generously provided by Matthey Bishop, Inc.

Reaction Conditions. The best reaction conditions for the formation of symmetrical 1,3-dienes were determined by employing the following general procedure. The appropriate amounts of palladium chloride (1 or 2 mmol) and anhydrous lithium chloride (2 or 4 mmol) were placed in a flask containing a nitrogen inlet tube and septum outlet. The flask was flushed with nitrogen and filled with 10 ml of the appropriate solvent and an appropriate hydrocarbon internal standard. After the reaction temperature (0 or 25 °C) was adjusted, 2 mmol of either styrylmercuric chloride or *trans*-1-hexenylmercuric chloride was added by means of a funnel through the top of the reaction flask while backflushing with nitrogen. The flask was then allowed to slowly warm to room temperature and stirred overnight. Ether (5 ml) was added and the reaction mixture was analyzed directly by GLC analysis on an SE-30 column. Product determinations were made by comparison with authentic samples. The exact amount of each reagent and the results are presented in Table I.

Effect of Phosphorus Compounds. The following standard procedure was employed. Palladium chloride (1 mmol) and either 0 or 4 mmol of anhydrous lithium chloride were placed in a flask under nitrogen. THF (10 ml), 4 mmol of the appropriate phosphorus compound, and approximately 0.1 g of octadecane as an internal standard were added and the flask cooled to 0 °C. Styrylmercuric chloride (2 mmol) was added with nitrogen backflushing. The flask was allowed to slowly warm to room temperature and stirred overnight. GLC analysis on an SE-30 column gave the results indicated in Table II.

Standard Procedure for the Synthesis of Dienes and Polyenes. The following procedure for the preparation of *trans,trans*-2,2,7,7-tetramethyl-3,5-octadiene is representative. To a well-dried nitrogen-filled flask with septum inlet were added 100 ml of HMPA, 40 mmol of anhydrous lithium chloride, and 10 mmol of palladium chloride. The flask was thoroughly cooled in an ice bath and 20 mmol of *trans*-3,3-dimethyl-1-butenylmercuric chloride was added rapidly while backflushing with nitrogen. The reaction mixture immediately turned black and was allowed to slowly warm to room temperature and then stirred overnight, at which time activated carbon, water, and pentane were added. After filtration the organic layer was separated and the aqueous layer repeatedly extracted with pentane. The combined extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated, leaving 1.60 g (96%) of a very pale yellow solid which was analytically pure by GLC and NMR analysis: mp 78–79 °C (EtOH); ^{1}H NMR (CCl_4) δ 1.02 (s, 18, CH_3) and 5.3–6.0 ppm (m, 4, vinyl). This compound was identical with an authentic sample.[3c]

The following compounds were prepared in a similar fashion. Dimethyl *cis,trans*- and *trans,trans*-10,12-docosadienedioate: mp ~40 °C (mixture of isomers by ^{1}H NMR and GLPC); ir (max) (neat) 2910, 2840, 1740, 1435, 1170, and 980 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.31 (m, 24, CH_2), 1.8–2.4 (m, 8, $CH_2C{=}O$ and $CH_2CH{=}$), 3.58 (s, 6, CH_3O), and 5.0–6.3 ppm (m, 4, vinyl); *m/e* 394.3079 ± 0.0020 (calcd for $C_{24}H_{42}O_4$, 394.3083). *cis,cis*-1,2,3,4-Tetraphenylbutadiene (use a benzene extraction): mp 182–184 °C (hexane–benzene) (lit.[26] mp 183 °C). (*E,E*)-2,5-Diacetoxy-3,4-dimethyl-2,4-hexadiene: mp 32.5–33.0 °C; ir (max) (neat) 2920, 1755, 1685, 1435, 1375, 1235, 1180, 1070, and 1015 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.57 (m, 6, allyl), 1.78 (m, 6, allyl), and 2.08 ppm (s, 6, $CH_3C{=}O$); *m/e* 226.1204 ± 0.0012 (calcd for $C_{12}H_{18}O_4$, 226.1205). *trans,trans*-2,7-Dimethyl-1,3,5,7-octatetraene: yellow oil; ir (max) (CCl_4) 3080, 3020, 2970, 2915, 1770, 1620, 1578, 1263, 1100, 985, and 885 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.73 (m, 6, CH_3), 4.84 (m, 4, vinyl), and 6.14 ppm (m, 4, vinyl) (each peak closely approaches a singlet but has some very slight splitting); λ_{max} (cyclohexane) 270, 281, 293, and 307 nm (same relative extinction coefficients as 1,3,5,7-octatetraene[15]); *m/e* 134.1094 ± 0.0007 (calcd for $C_{10}H_{14}$, 134.1096). (*E,E*)-4,5-Diethylidene-2,6-octadiyne: mp 95–96 °C; ir (max) (KBr) 3020, 2950, 2890, 2830, 2225, 1675, 1600, 1435, 1325, 935, 830, and 785 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.90 (d, 3, $J = 7$ Hz, allyl), 2.04 (s, 3, propargyl), and 6.28 ppm (q, 1, $J = 7$ Hz, vinyl); λ_{max} (hexane) 239 nm (ϵ 16 600), 246 (20 800), and 255 (17 600); *m/e* 158.1098 ± 0.0008 (calcd for $C_{12}H_{14}$, 158.1096). All reactions appear to proceed with very high stereospecificity as indicated by NMR and GLC analysis and described in the text. All other dienes were identified by comparison with authentic samples of all three possible stereoisomers prepared by alternate methods.

All GLC yields were determined on reactions run on one-tenth the above scale following a GLC analysis procedure identical with that outlined in the section entitled "Reaction Conditions". Internal standard correction factors were determined using authentic diene samples.

Alkyl- and Arylmercurial Dimerization Reactions. These reactions were run exactly as the above GLC diene reactions. Internal standard correction factors were determined using authentic hydrocarbon samples.

Attempted Catalysis. All attempted catalytic reactions were run according to our above GLC diene procedure. The cupric chloride reaction was run using the following reagents: styrylmercuric chloride (2 mmol), lithium chloride (2 mmol), anhydrous cupric chloride (4 mmol), palladium chloride (0.1 mmol), and HMPA (10 ml). The tetrakis(triphenylphosphine)palladium reactions were run using *trans*-1-hexenylmercuric chloride or styrylmercuric chloride (2 mmol), lithium chloride (0 or 4 mmol), tetrakis(triphenylphosphine)palladium (0.1 mmol), and HMPA (10 ml). All yields were determined using an appropriate hydrocarbon internal standard.

Acknowledgments. The author gratefully acknowledges both the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for their generous support of this research. A special debt of gratitude is due Professor George Zweifel, who generously provided numerous authentic diene samples, and Matthey Bishop, Inc. for a large gift of palladium chloride. The capable assistance of Mr. John C. Bernhardt in the arylmercury dimerization reactions is also greatly appreciated.

Registry No.—Dimethyl *cis,trans*-10,12-docosadienedioate, 58873-39-5.

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