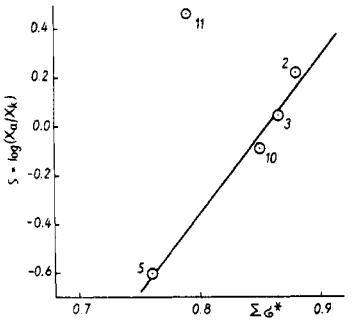

Figure 5. Polar effects on the selectivity (log X_a/X_b) for oxidation of $R^1R^2C{=}CH_2$ alkenes by thallium(III) nitrate in methanol at 25 °C. Values of σ^* are from ref 19. 23DMB1 is not included in correlation.

compounds will be favored. This trend may be seen from Tables I, II, and V. For $R^1R^2C{=}CH_2$ alkenes the yield of carbonyl compounds increases with increasing substituent bulk in the order 2MP1 < IB < 2MB1 < αMS < 2EH1 < 244TMP1 (for the oxidation in an aqueous medium, the steric factors dominate) or with increasing nucleophilicity in the order 2-chlorpropene (2CP) < 2EH1 < 2MB1 < 2MP2 < 2MH1 < 2,3-dimethyl-1-butene (23DMB1) (in methanol, the intrinsic nucleophilicity dominates), respectively.

In addition, from Table IV it can be seen that polar effects have influence on selectivity in the oxidation of internal alkenes by thallium(III) sulfate in aqueous medium and in the oxidation of $R^1R^2C{=}CH_2$ alkenes by thallium(III) nitrate in methanol.

Medium Effect. The selectivity data for oxidation of $R^1R^2C{=}CH_2$ alkenes by thallium(III) nitrate in methanol are listed in Table V and illustrated in Figure 5. By comparison of data for aqueous (Table I) and methanolic (Table V) mediums it is obvious that in methanol the product distribution is the reverse of that in water. The slope in Figure 5 has a relatively high absolute value. This is in agreement with direct addition to the C=C bond. The effect on the migration aptitude of alkyl groups, giving ketones, is decreased with electron-withdrawing substituents, which are suitable for formation of dimethoxy ether. This is the same situation as with the oxidation of terminal *n*-alkenes.[7b] We propose two possible explanations for this fact. In the simplest terms, we expect the transition state for alkyl group rearrangement (TS1) to be stabilized by an increase in the dielectric constant of the solvent. Thus, in a solvent with a higher dielectric constant (H_2O), formation of ketones would be preferred. It is also possible to interpret the data in terms of the HSAB principle.[20] TS1, TS2, and TS3 are species of nonclassical ion character. According to the HSAB principle, the less carbonium character a center attains during a reaction, the less hard of an acid it will be. Thus, nonclassical carbonium ions are less than hard acids. Methanol is a stronger nucleophilic agent than water (therefore a softer base), so it can better attack the oxythallic adduct with formation of the oxonium ion (TS2 and TS3), thus producing diethers and aldehydes. Simultaneously, electron-withdrawing substituents will decrease electron density at the C_2 atom of TS2, and thus an H^- shift, giving an aldehyde, will be favored. In accord with the reactivity–selectivity principle, the selectivity will be increased.

Conclusion

Oxidation of branched alkenes in aqueous medium gives substantially greater yields of carbonyl compounds than oxidation in methanol. Determination of T_{is} and the "inverse selectivity temperature" has great importance for planning a synthesis of carbonyl compounds and diols or diethers. Mechanistic application of the reactivity–selectivity principle to elucidation of the reaction mechanism of the oxidation of alkenes by thallic salts can lead to serious errors if temperature effects are disregarded.

Registry No. Isobutene, 115-11-7; 2-methyl-1-butene, 563-46-2; 2-methyl-1-pentene, 763-29-1; 2,4,4-trimethyl-1-pentene, 107-39-1; 2-ethyl-1-hexene, 1632-16-2; 2-methylstyrene, 98-83-9; 2-methyl-2-pentene, 625-27-4; trans-4-methyl-2-pentene, 674-76-0; 2,4,4-trimethyl-2-pentene, 107-40-4; $Tl_2(SO_4)_3$, 16222-66-5; $Tl(NO_3)_3$, 13746-98-0.

Reactions of π-Allylic Palladium Intermediates with Amines

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Several dimeric π-allylic palladium chloride complexes have been prepared by addition of aryl-, hydrido-, and (carbomethoxy)palladium chlorides, prepared in situ, to various conjugated dienes. Stoichiometric reactions of several of these complexes with secondary amines were carried out and the influence of added ligands and changes in the anions in the complexes on the reactions were noted. The stoichiometric reactions were then compared to similar catalytic reactions. The evidence suggests that the products formed in the palladium-catalyzed reactions of aryl iodides and bromides with conjugated dienes and secondary amines to form arylated dienes and allylic amines involve π-allylic palladium complexes as intermediates.

The palladium-catalyzed reaction of aryl halides with conjugated dienes and triethylamine produces arylated dienes.[1] The reactions, at least partly, appear to proceed by way of π-allylic palladium complexes which undergo elimination in the final step. π-Allylic palladium complexes are also believed to be intermediates in the palladium-catalyzed reaction of vinylic halides with olefins and amines.[2-4] In many of these reactions the intermediates are resistant to elimination particularly when an aryl,

(1) B. A. Patel, J. E. Dickerson, and R. F. Heck, *J. Org. Chem.*, **43**, 5018 (1978).

(2) H. A. Dieck and R. F. Heck *J. Org. Chem.*, **40**, 1083 (1975).

(3) R. C. Larock and M. A. Mitchell, *J. Am. Chem. Soc.*, **98**, 6718 (1976).

(4) B. A. Patel and R. F. Heck, *J. Org. Chem.*, **43**, 3898 (1978).

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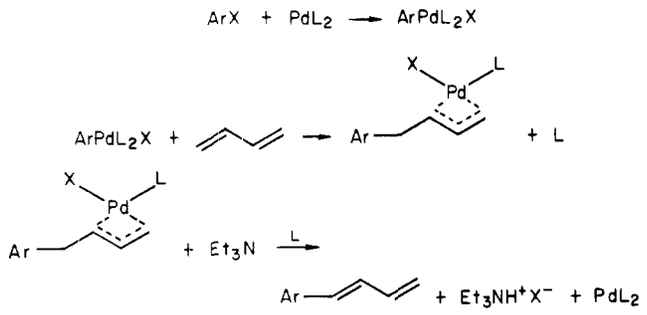
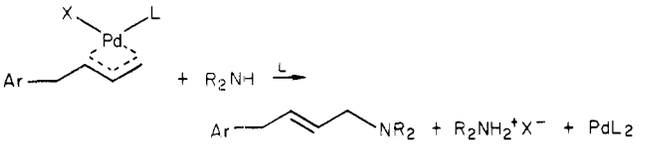


carboxyl, or nitrile substituent is *not* on a carbon adjacent to one of the terminal carbons of the π-allylic palladium group. In these resistent cases, catalytic reactions occur if the π-complexed intermediates are decomposed by nucleophilic reactions with secondary amines. This modification produces allylic amines rather than dienes as products.

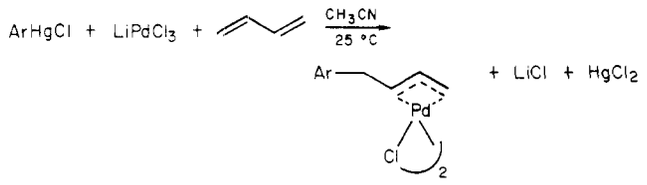


The details of the mechanism of the catalytic reaction are of interest since they determine the products and their sterochemistry. Accordingly, we have prepared a variety of π-allylic palladium complexes and investigated their reactions with amines. We also studied the related catalytic reactions in which the isolated π complexes were the expected intermediates. It is known from studies of Akermark that dimethylamine forms crotyldimethylamine with π-crotylpalladium chloride dimer;[5] however, this complex was only investigated with the one amine.

The questions we wished to answer in this study were the following. (1) Do amine substitution and hydride elimination occur from the π-allylic complex only or are dienes formed without intervention of a π-allylic complex? (2) Can these reactions be influenced significantly by addition of arylphosphines? (3) How selective is the nucleophilic attack of the amine on unsymmetrically substituted π-allylic complexes?

Results and Discussion

Preparation of π-Allylic Palladium Complexes. The complexes prepared are listed in Table I. The chloro-bridged dimers, with one exception, were prepared by basically the same reaction, the addition of "aryl-", "hydrido-", or "(carbomethoxy)palladium chloride" to conjugated dienes. The necessary palladium compounds are unstable and were prepared in situ from organomercurials and palladium chloride. This reaction employing phenylmercuric chloride was reported earlier,[6] but several new examples are reported here. Mixtures of the arylmercuric chloride, lithium chloropalladate, and the diene are stirred at room temperature in acetonitrile solution to produce the complexes in low to high yields. The yields are also given in Table I.

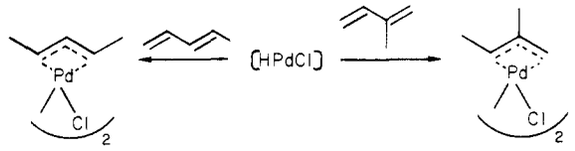


(5) B. Akermark and K. Zetterberg, *Tetrahedron Lett.*, 3733 (1975).
(6) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5542 (1968).

Most of our study was conducted with phenylmercuric chloride, but we did look at two other arylmercurials to show the generality of the reaction. Both 3-(chloromercuri)benzaldehyde and 2,4-dimethoxyphenylmercuric chloride reacted with lithium chloropalladate and isoprene to form the expected adducts although the yields were only about 20% of theory. The low yields are probably in part, at least, due to the impure mercurials used since it is difficult to purify these compounds. A variation of the reaction occurs when alkylmercurials with at least one sp^3 bonded hydrogen β to the mercury are used. In these cases the intermediate alkylpalladium chloride apparently undergoes a very rapid β-hydride elimination forming olefin and hydridopalladium chloride. The last species seems to be stable long enough to react with the diene present and form the π-allylic palladium chloride dimers in reasonable yields, at least, with isoprene and 1,3-pentadiene. An

$$n\text{-}C_4H_9HgCl + LiPdCl_3 \rightarrow [n\text{-}C_4H_9PdCl] + HgCl_2 + LiCl$$

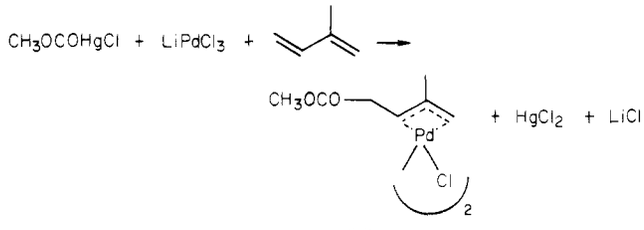
$$[n\text{-}C_4H_9PdCl] \rightarrow [HPdCl] + n\text{-}C_4H_8$$



(75%) (39%)

attempt to employ 2,4-dimethyl-1,3-pentadiene in this section failed, presumably because of the low reactivity of disubstituted terminal double bonds toward addition of the hydride.

Another variation of this reaction was used to prepare carbomethoxy-substituted π-allylic complexes. (Carbomethoxy)mercuric chloride was reacted with lithium chloropalladate and the diene to accomplish this. Two dienes were tried, isoprene and 1,3-cyclohexadiene. The products of these reactions were relatively unstable and only low yields of the π-allylic complexes were obtained.



21%

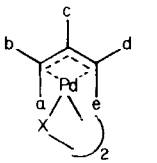
Complex XII (see Table I for compound numbers) was obtained in 65% yield from the olefin, 2-methyl-1-pentene, and palladium chloride by the procedure of Trost.[7]

The bromo and iodo π-allylic palladium complexes listed in Table I were prepared from the π-allylic palladium acetate dimers and the appropriate lithium halide. The acetates were obtained from the π-allylic chlorides and silver acetate.

Attempts were made to isolate tri-*o*-tolylphosphine complexes of some of the π-allyl palladium derivatives. While crystalline complexes were easily isolated from reactions of the phosphine and the dimeric chloro complexes,

(7) B. M. Trost, P. E. Strege, L. Weber, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, **100**, 3407 (1978).
(8) B. A. Patel, L. Kao, N. A. Cortese, J. V. Minkiewicz, and R. F. Heck, *J. Org. Chem.*, **44**, 918 (1979).
(9) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5518 (1968).
(10) W. Schoeller, W. Schrauth, and W. Essers, *Chem. Ber.*, **46**, 2864 (1913).

Table I. π-Allylic Palladium Complexes and Their Reactions with Amines[a]



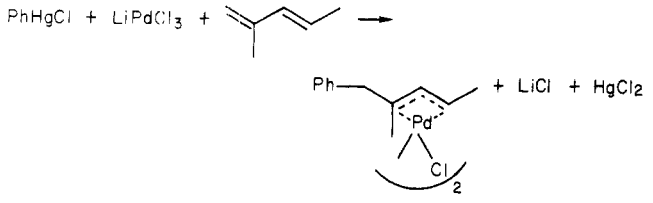
compd	anion X	complex a	b	c	d	e	% yield[b]	amine[c]	reaction time, h	temp, °C	product	% yield (by GLC)
I	Cl	H	$C_6H_5CH_2$	CH_3	H	H	58	NEt_3	24	26	(*E*)-PhCH=CHC(CH_3)=CH_2	63
											$PhCH_2CH=C(CH_3)_2$	6
											$Ph(CH_2)_2CH(CH_3)_2$	10
I	Cl	H	$C_6H_5CH_2$	CH_3	H	H		P*H	3	26	(*E*)-PhCH=CHC(CH_3)=CH_2	43
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$P*	30
											$Ph(CH_2)_2CH(CH_3)_2$	13
I	Cl	H	$C_6H_5CH_2$	CH_3	H	H		P*H	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	70
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$P*	18
I	Cl[d]	H	$C_6H_5CH_2$	CH_3	H	H		P*H	2	100	(*E*)-PhCH=CHC(CH_3)=CH_2	62
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$P*	25
											$Ph(CH_2)_2CH(CH_3)_2$	8
I	Cl	H	$C_6H_5CH_2$	CH_3	H	H		MH, *i*-Pr_2NEt[e]	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	55
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$M	11
											reduced dienes	30
I	Cl	H	$C_6H_5CH_2$	CH_3	H	H		MH, *i*-Pr_2NEt[f]	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	52
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$M	20
											reduced dienes	28
I	Cl[g]	H	$C_6H_5CH_2$	CH_3	H	H		P*H[h]	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	57
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$P*	25
											reduced dienes	8
I	Cl[i]	H	$C_6H_5CH_2$	CH_3	H	H		P*H[h]	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	42
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$P*	13
											reduced dienes	8
I	Cl[j]	H	$C_6H_5CH_2$	CH_3	H	H		P*H[h]	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	51
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$P*	36
											reduced dienes	5
I	Cl[k]	H	$C_6H_5CH_2$	CH_3	H	H		P*H[h]	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	29
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$P*	27
											reduced dienes	8
I	Cl[l]	H	$C_6H_5CH_2$	CH_3	H	H		P*H[h]	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	46
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$P*	19
											reduced dienes	6
I	Br	H	$C_6H_5CH_2$	CH_3	H	H	72[h]	P*H[h]	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	62
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$P*	19
											reduced dienes	15
I	Br[d]	H	$C_6H_5CH_2$	CH_3	H	H		P*H[h]	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	9
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$P*	52
											reduced dienes	40
I	I	H	$C_6H_5CH_2$	CH_3	H	H	70[n]	P*H[h]	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	62
											(*E*)-$PhCH_2CH=C(CH_3)CH_2$P*	30
											$PhCH_2CH=C(CH_3)_2$	5
											$PhCH_2CH_2CH(CH_3)_2$	1

I	I[d]	H	$C_6H_5CH_2$	CH_3	H	H		P*H[h]	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	35
											(*E*)-$PhCH_2CH$=C(CH_3)CH_2P*	50
											reduced dienes	8
I	OAc	H	$C_6H_5CH_2$	CH_3	H	H		P*H[h]	1	100	(*E*)-PhCH=CHC(CH_3)=CH_2	50
											(*E*)-$PhCH_2CH$=(CH_3)CH_2P*	4
											reduced dienes	19
II	Cl	H	3-$OCHC_6H_4CH_2$	CH_3	H	H	20					
III	Cl	H	2,4-$(CH_3O)_2C_6H_3CH_2$	CH_3	H	H	22					
IV	Cl	CH_3	$C_6H_5CH_2$	CH_3	H	H	63	MH	1	100	(*E*)-PhCH=C(CH_3)C(CH_3)-=CH_2	31
											$PhCH_2C(CH_3)$=C(CH_3)CH_2M	31
V	Cl	CH_3	$C_6H_5CH_2$	H	CH_3	H	44					
VI	Cl	H	$C_6H_5CH_2$	CH_3	CH_3	H	33					
VII	Cl	H	$C_6H_5CH_2$	H	CH_3	CH_3	96	MH	1.5	100	(*E*)-PhCH=CHCH=C(CH_3)$_2$	40
											(*E*)-$PhCH_2CH$=CHC(CH_3)-=CH_2	6
											(*E*)-$PhCH_2CH$=CHC(CH_3)$_2$M	45
VII	Cl[d]	H	$C_6H_5CH_2$	H	CH_3	CH_3		MH	1	100	(*E*)-PhCH=CHCH=C(CH_3)$_2$	38
											$PhCH_2CH$=CHC(CH_3)=CH_2	7
											$PhCH_2CH$=CHC(CH_3)$_2$M	43
VII	Br[d]	H	$C_6H_5CH_2$	H	CH_3	CH_3	83[i]	MH	1	100	(*E*)-PhCH=CHCH=C(CH_3)$_2$	54
											(*E*)-$PhCH_2CH$=CHC(CH_3)$_2$M	45
VII	Br[d]	H	$C_6H_5CH_2$	H	CH_3	CH_3		MH	1	100	(*E*)-PhCH=CHCH=C(CH_3)$_2$	43
											(*E*)-$PhCH_2CH$=CHC(CH_3)$_2$M	53
VII	I	H	$C_6H_5CH_2$	H	CH_3	CH_3	75[m]	MH[h]	2	100	(*E*)-PhCH=CHCH=C(CH_3)$_2$	54
											(*E*)-$PhCH_2CH$=CHC(CH_3)$_2$M	20
VII	I[d]	H	$C_6H_5CH_2$	H	CH_3	CH_3		MH[h]	1	100	(*E*)-PhCH=CHCH=C(CH_3)$_2$	80
											(*E*)-$PhCH_2CH$=CHC(CH_3)$_2$ M	8
VII	OAc	H	$C_6H_5CH_2$	H	CH_3	CH_3	79[n]	MH	1	100	(*E*)-$PhCH_2CH$=CHC(CH_3)$_2$M	99
VII	Cl	H	$C_6H_5CH_2$	H	CH_3	CH_3		P*H	1	100	(*E*)-PhCH=CHCH=C(CH_3)$_2$	93
VII	Cl	H	$C_6H_5CH_2$	H	CH_3	CH_3		P*H	1	100	$Ph(CH_2)_3CH(CH_3)_2$	50
											(*E*)-PhCH=CHCH=C(CH_3)$_2$	11
											(*E*)-$PhCH_2CH$=CHC(CH_3)$_2$M	
											reduced dienes	11
VIII	Cl	H	$C_6H_5(CH_3)CH$	H	CH_3	H	33	MH	0.5	100	$Ph(CH_3)$CHCH=CHC(CH_3)M	61
											dienes	10
IX	Cl	H	$C_6H_5(CH_3)CH$	H	$(CH_2)_2CH_3$	H	51					
X	Cl	H	$C_6H_5(CH_3)CH$	H	CO_2CH_3	H	74					
XI	Cl	CH_3	$C_6H_5CH_2$	H	CH_3	CH_3	49					
XII	Cl	H	CH_3CH_2	CH_3	H	H	65	MH	0.1	50	CH_3CH_2CH=C(CH_3)CH_2M	43
XII	Cl[d]	H	CH_3CH_2	CH_3	H	H	45	MH	2	100	CH_2=C(CH_3)CH=$CHCH_3$	13
											$MCH_2C(CH_3)$=$CHCH_2CH_3$	72
XIII	Cl	H	CH_3	CH_3	H	H	39					
XIV	Cl	H	CH_3	H	CH_3	H	75					
XV	Cl	H	$CH_3O_2CCH_2$	CH_3	H	H	21					
XVI	Cl	$CH_3OCOCHCH_2CH_2$-e (a)	H	H	H	e-$CH_2CH_2CHCO_2CH_3$ (a)	2					
XVII	Cl	H	$C_6H_6CH(CO_2CH_3)$	H	CH_3	CH_3	25[p]					

[a] Reaction mixtures were composed of 0.5 mmol of dimeric palladium complex and 15 mmol of amine unless otherwise noted. [b] Based upon palladium chloride. [c] P*H = piperidine, MH = morpholine. [d] 1 mmol of tri-*o*-tolylphosphine was added per 0.5 mmol of the dimeric palladium complex. [e] A mixture of 1 mmol of morpholine and 2 mmol of diisopropylethylamine was used per 0.5 mmol of the dimeric palladium complex. [f] A mixture of 2 mmol of morpholine and 2 mmol of diisopropylethylamine was used per 0.5 mmol of the dimeric palladium complex. [g] 1 mmol of dipyridyl added per 0.5 mmol of dimeric palladium complex. [h] Only 2.5 mmol of amine was used per 0.5 mmol of the dimeric palladium complex and 2 mL of acetonitrile also was added. [i] 2 mmol of triethylphosphine added per 0.5 mmol of dimeric palladium complex. [j] 2 mmol of triphenylphosphine added per 0.5 mmol of dimeric palladium complex. [k] 6 mmol of triphenylphosphine added per 0.5 mmol of dimeric palladium complex. [l] 1 mmol of 1,2-bis(diphenylphosphino)ethane added per 0.5 mmol of dimeric palladium complex. [m] Yield based upon the π-allylic palladium acetate. [n] Yield based upon the π-allylic palladium chloride. [o] Yield of bis(tri-*o*-tolylphosphine)complex isolated. [p] Obtained as a mixture with another isomeric complex produced in 8% yield.

they were very difficult to obtain analytically pure. Therefore, for most of our studies we simply added the necessary phosphine or other required ligand to the π-allylic complexes and assumed the phosphine derivatives formed rapidly in situ. We preferred the tri-*o*-tolylphosphine ligand to less hindered phosphines in order to avoid a possible competing reaction forming phosphonium salts.[11]

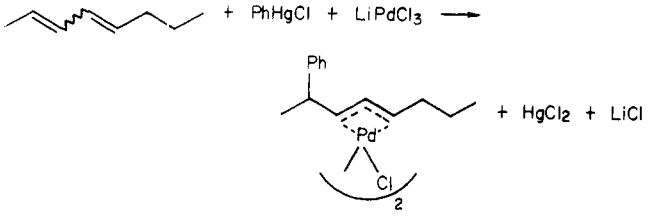
Structures of π-Allylic Palladium Complexes. The dienes which were not conjugated with ester groups all reacted exclusively with aryl-, hydrido-, or (carbomethoxy)palladium chlorides to place the aryl, hydrogen, or carbomethoxy groups on the terminal carbon of the least substituted double bond of the diene system. If there was a choice between a 1,2-disubstituted double bond and a 2,2-disubstituted one, the last structure was preferred. Thus, 2-methyl-1,3-pentadiene with phenylmercuric chloride and lithium chloropalladate reacted to form only the (1-benzyl-1,3-dimethyl-π-allyl)palladium chloride dimer, compound V (44% yield).



44%

V

The 1,2-disubstituted double bonds also will react if more reactive double bonds are absent. For example, a cis–trans mixture of 2,4-octadiene and "phenylpalladium chloride" produced the [1-(α-methylbenzyl)-3-*n*-propyl-π-allyl]palladium chloride dimer, compound IX, 51% yield.

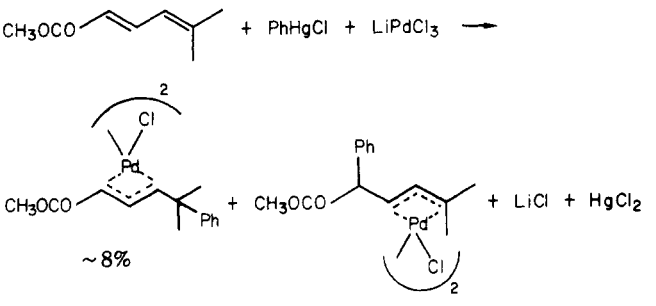


51%

IX

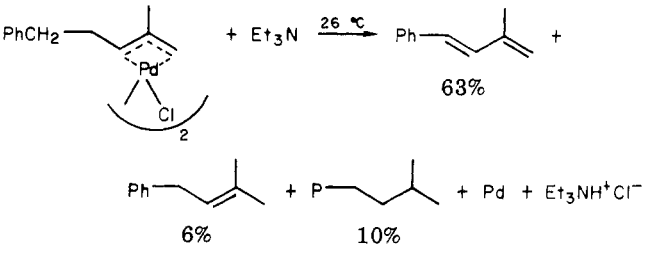
The phenyl group added exclusively to the less hindered second carbon of the 2,4-octadiene. Therefore, the order of reactivity of the diene double bonds toward "phenylpalladium chloride" is CH_2=CHR > CH_2=CR_2 > RCH=CHR. The selectivity of the addition is believed to occur because the less substituted double bonds coordinate more easily with the arylpalladium halides and therefore addition occurs there placing the large organic group on the least substituted position.

The selectivity of the "phenylpalladium chloride" attack on diene systems conjugated with ester functions is not as high. Methyl sorbate reacts to give a single π complex with the phenyl attached to carbon 5 of the sorbate group (74% yield, compound X), but catalytic experiments described below show that some attack also occurs at carbon 3 and this material does not yield a stable π-allylic complex. (*E*)-Methyl 5-methyl-2,4-hexadienoate, on the other hand, yields a mixture of about 25% of the 5-phenylated compound and 75% of the 2-phenylated product, compound XVII (total yield, 33%).

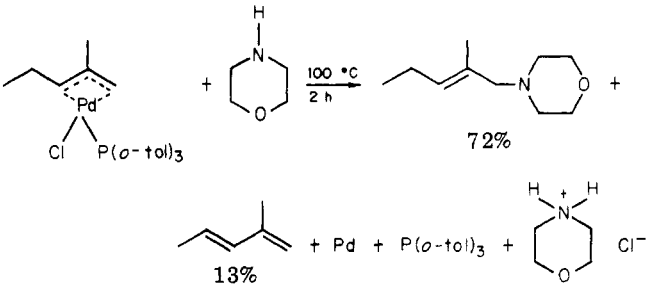


XVII

Reactions of π-Allylic Complexes with Amines. Most of the π-allylic palladium complexes prepared were reacted with either or both piperidine and morpholine to determine the position of attack of the amine and to compare these results with those of the catalytic reactions described below. The results of the stoichiometric reactions are given in Table I. In general, mixtures of conjugated dienes and allylic amines were obtained, although in a few examples only dienes were formed and in a few others olefins and/or alkanes were also formed. For comparison compound I-Cl was also reacted with triethylamine. After 24 h at 26 °C complete reaction had occurred, producing 63% of the expected phenyl diene and 16% of reduced dienes.



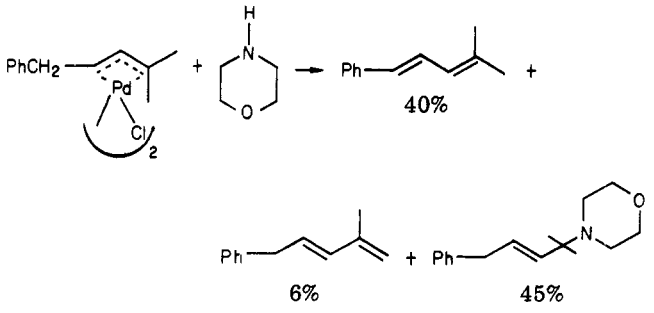
The allylic amines formed, in all cases, can be explained as the result of S_N2 attacks of morpholine or piperidine on the π-allylic carbon furthest removed from the aromatic group. In the example where the phenyl substituent was absent, compound XII, the amine attacked the monosubstituted π-allylic carbon rather than the secondary one.



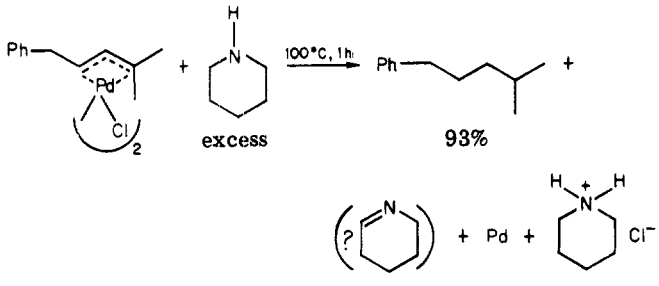
The major or exclusive dienes formed in the amine reaction with phenylated compounds were the phenyl-conjugated isomers. Only in the reaction of complex VII-Cl did we find and identify another isomer, the terminal conjugated diene. In this and other examples the allylic amine products were observed to undergo pyrolysis in the gas chromatograph to form a diene different than the one formed directly. The amines were removed from the product mixtures by cold aqueous acid extraction before the dienes were analyzed by GLC to be sure this was not happening. The dienes were stable under the conditions of the analysis.

The partially or totally reduced diene products observed in several reactions apparently are being formed by a

(11) C. B. Ziegler, Jr., and R. F. Heck, *J. Org. Chem.*, 43, 2941 (1978).



palladium-catalyzed hydrogen-transfer reduction. The source of the hydrogen must be the amine since reducing the concentration of amine decreases the yield of reduced dienes. The most serious problem occurred with VII-Cl where 15 mmol of piperidine and 0.5 mmol of dimeric palladium complex at 100 °C for 1 h gave only the totally saturated product (93%).



When the same reaction was carried out with only 2.5 mmol of amine, 50% of the phenyl diene, 11% of the amine derivative, and only 11% of reduced products were obtained.

The anion in the π-allylic complex can have a significant effect upon the products formed in the reaction with the amines, particularly with regard to the diene to amine adduct ratio. Reactions of compounds I and VII with Cl, Br, and I anions were compared. For compound I, 30% amine adduct was obtained with the iodide and only 18–19% with the chloride or bromide. With compound VII the iodide gave only 20% amine adduct while the bromide and chloride each gave 45%. The acetate of VII under the same conditions gave only the phenylated diene. We also investigated the influence of organophosphines, and in one case dipyridyl, upon the amino reactions. These effects were also significant in some cases but as yet unpredictable. In some instances the addition of a phosphine had little effect but in others the effect was large. For example, I-Cl showed little change in the ratio of diene to amine adduct when 2 mmol of tri-*o*-tolylphosphine was added, while the I-Br product ratio changed from 62:19 diene–amine adduct to 9:52.

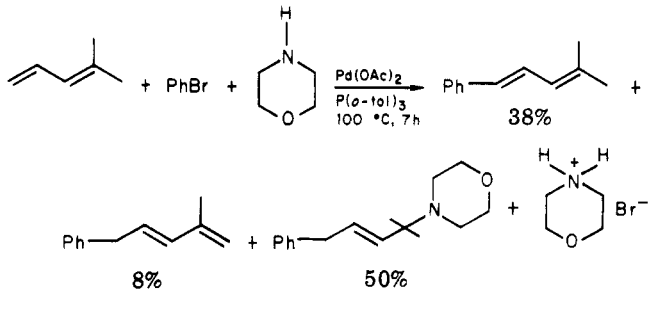
Catalytic Reactions. The catalytic reactions employing bromobenzene were carried out under conditions as similar as possible to the stoichiometric reactions in several instances to determine if the products formed could have arisen from the π-allylic palladium intermediate in the catalytic examples. Other variations were tried to better define this useful synthetic reaction. The results of our catalytic studies are given in Table II.

A significant difference from the stoichiometric reactions is the absence of reduced dienes in any of the catalytic reactions. This is probably due to the fact that the palladium concentration relative to the products is much lower in the catalytic reactions and the hydrogen-transfer reduction, therefore, is much slower.

The first reaction in Table II, the phenylation of isoprene with iodobenzene and triethylamine, employed 5 mol % palladium acetate and 10 mol % triphenylphosphine. The large amount of catalyst was used because the yield of the diene was less with smaller amounts of catalyst. The longer reaction time necessary with the lower catalyst level caused some polymerization of the diene. The same reaction with 1 mol% palladium acetate and 2 mol % tri-*o*-tolylphosphine with piperidine as the base gave a much higher yield of products even though a longer reaction time was required (51 vs. 18 h). The products were 22% of the phenylated diene and 59% of the amine adduct. This compares with the 35% yield of diene and 50% yield of the amine adduct obtained in the related stoichiometric reaction with complex I-I. Similar agreement was obtained from the reactions done in the absence of phosphine. The catalytic reaction gave 54% diene and 39% amine adduct and the stoichiometric reaction gave 62% diene and 30% amine. The related bromide reactions with phosphine were similar. The catalytic reaction produced 29% diene and 69% amine adduct while stoichiometrically the yields were 9% diene and 52% amine adduct with 40% reduced dienes. In the absence of phosphine the catalytic yields were 57% diene and 35% amine adduct and the stoichiometric yields were 62% diene and 19% amine with 15% reduced products also. Since the reduced products could be arising from either or both direct products, not much can be said about the comparisons in the bromide reactions. It is clear, however, that considerably more amine adduct is produced from either bromo- or iodobenzene in the presence of tri-*o*-tolylphosphine than in its absence. This effect is also observable in several other examples in Tables I and II.

We looked at the catalytic reaction of (*E*)-1,3-pentadiene with bromobenzene with three different phosphines and without a phosphine to determine how much the yield of the amine adduct could be influenced by this change. Tri-*o*-tolyl-, tris(*m*-chlorophenyl)- and tris(2,3,4,5-tetramethylphenyl)phosphines were rather similar in the reaction within about ±5% of the yield of the amine adduct, and this was about the same yield obtained in the absence of a phosphine.

Considerable data was collected on the phenylation of 4-methyl-1,3-pentadiene. In a very slow reaction at 100 °C with diethylamine as the base and 2 mol % palladium acetate and 6 mol % tri-*o*-tolylphosphine as catalyst, the reaction produced 64% of the phenyl-conjugated diene, 11% of the terminal diene, and no amine adduct. While with morpholine as the base a rapid reaction occurred forming 38% of the phenyl-conjugated diene, 8% of the terminal diene, and 50% of the amine adduct.



In the absence of a phosphine, the morpholine reaction produced 68% phenyl-conjugated diene and 9% terminal diene. If the bromobenzene–4-methyl-1,3-pentadiene reaction is carried out in the presence of tetrabutylammonium iodide and tri-*o*-tolylphosphine, only dienes are produced. This result is also obtained when iodobenzene is reacted under the same conditions or in the presence of tetrabutylammonium bromide. It is not clear

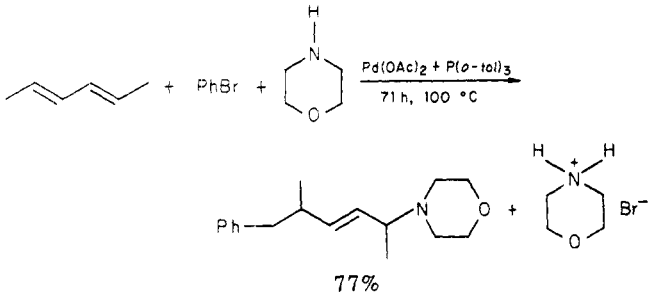
Table II. Palladium-Catalyzed Reactions of Bromobenzene with Various Dienes

diene	amine[a]	PR_3[b]	reaction time, h	temp, °C	products	% yield (by GLC)
isoprene[c,d]	NEt_3	10% PPh_3[e]	18	100	(*E*)-PhCH=CHC(CH_3)=CH_2	52
isoprene	P*H	2% P(*o*-tol)$_3$	25	100	(*E*)-PhCH=CHC(CH_3)=CH_2	29
					$PhCH_2CH=C(CH_3)CH_2P^*$	69
isoprene	P*H		72	100[f]	(*E*)-PhCH=CHC(CH_3)=CH_2	42
					(*E*)-$PhCH_2CH=CH(CH_3)$-CH_2P^*	12
isoprene[d]	P*H	2% P(*o*-tol)$_3$	13	100	(*E*)-PhCH=CHC(CH_3)=CH_2	22
					(*E*)-$PhCH_2CH=C(CH_3)CH_2P$	59
isoprene[d]	P*H		51	100	(*E*)-PhCH=CHC(CH_3)=CH_2	54
					(*E*)-$PhCH_2CH=C(CH_3)CH_2P$	39
(*E*)-1,3-pentadiene	P*H	2% P(*o*-tol)$_3$	18	100	(*E,E*)-PhCH=CHCH=CHCH$_3$	22
					(*E*)-$PhCH_2CH=CHCH(P^*)$-CH_3	55
(*E*)-1,3-pentadiene	P*H		22	100	(*E,E*)-PhCH=CHCH=CHCH$_3$	49
					(*E*)-$PhCH_2CH=CHCH(P^*)$-CH_3	45
(*E*)-1,3-pentadiene	P*H	2% P(*m*-ClC_6H_4)$_3$	46	100	(*E,E*)-PhCH=CHCH=CHCH$_3$	43
					(*E*)-$PhCH_2CH=CHCH(P^*)$-CH_3	53
(*E*)-1,3-pentadiene	P*H	2% P(2,3,4,5-$(CH_3)_4C_6H$)$_3$	46	100	(*E,E*)-PhCH=CHCH=CHCH$_3$	53
					(*E*)-$PhCH_2CH=CHCH(P^*)$-CH_3	38
2,3-dimethyl-1,3-butadiene[g]	MH	4% P(*o*-tol)$_3$[h]	75	125	(*E*)-PhCH=C(CH_3)C(CH_3)-$=CH_2$	18
					$PhCH_2C(CH_3)=C(CH_3)CH_2M$	32
(*E*)-3-methyl-1,3-pentadiene	MH	4% P(*o*-tol)$_3$[h]	38	100	(*E,E*)-PhCH=CHC(CH_3)-$=CHCH_3$	55
					$PhCH_2CH=C(CH_3)CH$-$(CH_3)M$	33
4-methyl-1,3-pentadiene	Et_2NH	6% P(*o*-tol)$_3$[i]	50	100	(*E*)-PhCH=CHCH=C(CH_3)$_2$	64
					(*E*)-$PhCH_2CH=CHC(CH_3)$-$=CH_2$	11
4-methyl-1,3-pentadiene	MH	6% P(*o*-tol)$_3$[i]	7	100	(*E*)-PhCH=CHCH=C(CH_3)$_2$	38
					(*E*)-$PhCH_2CH=CHC(CH_3)$-$=CH_2$	8
4-methyl-1,3-pentadiene[j,d]	MH		13	100	(*E*)-$PhCH_2CH=CHC(CH_3)_2M$	50
					(*E*)-PhCH=CHCH=C(CH_3)$_2$	68
					(*E*)-$PhCH_2CH=CHC(CH_3)$-$=CH_2$	9
4-methyl-1,3-pentadiene[k]	MH	4% P(*o*-tol)$_3$[h]	24	100	(*E*)-PhCH=CHCH=C(CH_3)$_2$	50
4-methyl-1,3-pentadiene[d]	MH	2% P(*o*-tol)$_3$	10	100	(*E*)-PhCH=CHCH=C(CH_3)$_2$	76
					(*E*)-$PhCH_2CH=CHC(CH_3)$-$=CH_2$	10
4-methyl-1,3-pentadiene[l]	MH	4% P(*o*-tol)$_3$[h]	24	100	(*E*)-PhCH=CHCH=C(CH_3)$_2$	97
(*E,E*)-2,4-hexadiene[m]	MH	2% P(*o*-tol)$_3$	96	100	(*E*)-$PhCH(CH_3)CH=CHCH$-$(M)CH_3$	69
(*E,Z*)-2,4-hexadiene[m]	MH	4% P(*o*-tol)$_3$[h]	71	100	(*E*)-$PhCH(CH_3)CH=CHCH$-$(M)CH_3$	77
methyl sorbate	NEt_3	4% P(*o*-tol)$_3$[h]	117	100	(*E,E*)-PhC(CH_3)=CHCH-$=CHCO_2CH_3$	34
					$CH_3CH=CHC(Ph)=CHCO_2$-CH_3	25
2,4-dimethyl-1,3-pentadiene	MH	4% P(*o*-tol)$_3$[h]	20 days	100	(*E*)-$PhCH_2C(CH_3)=CHC(CH_3)$-$=CH_2$	11
					(*E*)-PhCH=C(CH_3)CH=C-$(CH_3)_2$	30
2,4-octadiene[n]	MH	4% P(*o*-tol)$_3$[h]	87	100	(*E*)-$PhCH(CH_3)CH=CHCH$-$(M)(CH_2)_2CH_3$	26
					(*E*)-$PhCH(CH_3)CH(M)CH$-$=CH(CH_2)_2CH_3$	26
					2-phenyloctadienes	30
(*E*)-methyl 5-methyl-2,4-hexadienoate[d]	Et_3N		51	100	methyl 5-methyl-2-phenyl-2,4-hexadienoate	95[o]

[a] MH = morpholine, P*H = piperidine. [b] The percent PR_3 is based upon the bromobenzene used. Palladium acetate (1 mmol %) was employed except where noted. [c] Data taken from ref 1. [d] Iodo- rather than bromobenzene was used and 4 mL of acetonitrile was the solvent. [e] 5 mol % $Pd(OAc)_2$ and 10 mol % triphenylphosphine was used as the catalyst and iodobenzene rather than bromobenzene was used with 4 mL of acetonitrile. [f] 2 mol % $Pd(OAc)_2$ was used and reaction was only 65% complete at this time. [g] Reaction carried out by L.-C. Kao with iodo- rather than bromobenzene. [h] 2 mol % $Pd(OAc)_2$ and 4 mol % P(*o*-tol)$_3$ was used as catalyst. [i] 2 mol % $Pd(OAc)_2$ and 6 mol % P(*o*-tol)$_3$ was used as catalyst. [j] 1 mol % $Pd(OAc)_2$ and 4 mL of acetonitrile used. [k] 3 equiv of $(n\text{-}Bu)_4N^+I^-$ added with 4 mL of acetonitrile. Only about 65% complete when reaction stopped. [l] 3 equiv of $(n\text{-}Bu)_4N^+Br^-$ added with 4 mL of acetonitrile and iodo- rather then bromobenzene was used. [m] Only about 90% of the bromobenzene reacted. Yields are not corrected for the unreacted halide. [n] Cis-trans mixture (composition not determined). [o] Product contained about 20% of another compound with identical GLC retention time presumed to be methyl 5-methyl-5-phenylhexenoate from its NMR spectrum.

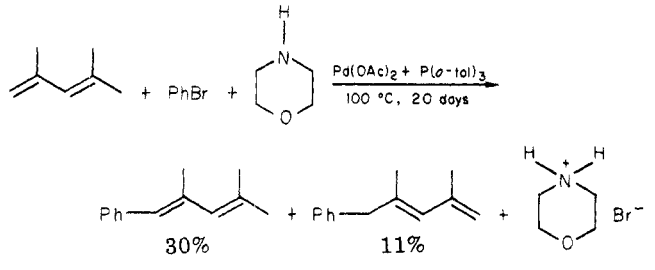
if this is simply a "salt effect" or whether iodide is the preferred halide in the intermediate π-allylic complex.

Both (*E,E*)- and (*E,Z*)-2,4-hexadiene react catalytically with bromobenzene and morpholine slowly to form only amine adduct in 60–77% yield. (In both reactions about 90% of the bromobenzene was used and the reactions appeared to stop).

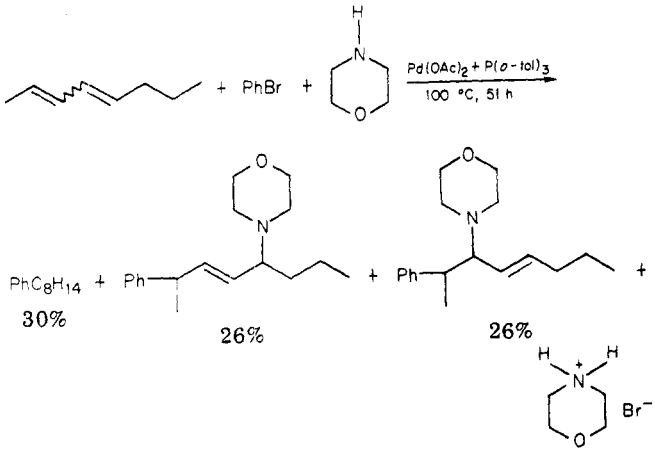


Methyl sorbate and bromobenzene react very slowly with triethylamine as the base with tri-*o*-tolylphosphine–palladium acetate catalyst to from a mixture of methyl 5-phenyl- and methyl 3-phenyl-2,4-hexadienoates in 34 and 25% yields, respectively. The phenylpalladium group apparently adds easily to either double bond in this ester conjugated system.

2,4-Dimethyl-1,3-pentadiene was the most unreactive diene we investigated. It reacted with bromobenzene and morpholine with a tri-*o*-tolylphosphine–palladium acetate catalyst over a period of 20 days at 100 °C to give only 30% of the phenyl-conjugated diene and 11% of the terminal diene.

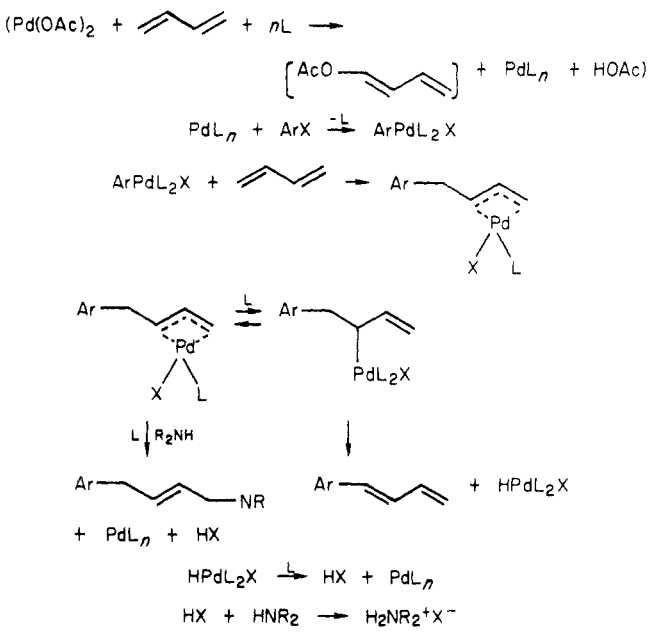


2,4-Octadiene (*E,Z* mixture) and bromobenzene with morpholine gave a mixture of phenyloctadienes and two allylically isomeric 2-phenyloctenylamines. Hydrogenation



of the phenyloctadienes produced only 2-phenyloctane. Thus, phenyl addition only occurs at the second carbon atom of the 2,4-octadiene system. The π-allylic palladium chloride intermediate, however, reacts equally well with the amine at either of the two terminal carbons of the π-allylic system.

Scheme I



The (*E*)-methyl 5-methyl-2,4-hexadienoate has a *gem*-dimethyl group on the end of the conjugated system and does not undergo addition at this position as easily as it does at carbon 2, and therefore phenylation with iodobenzene gives largely methyl 5-methyl-2-phenyl-2,4-hexadienoate. The product is not competely pure, however, and NMR evidence indicates the presence of a small amount of another product, possibly a methyl 5-methyl-5-phenylhexenoate.

Mechanism of Catalytic Phenylation of Dienes. From the data obtained, it appears that the products formed in the catalytic reactions can be explained by a mechanism involving the π-allylic palladium halide complexes as intermediates which may either undergo substitution at an allylic position with the amine to form allylic amine or elimination to form conjugated dienes. The evidence is not completely conclusive, but it appears that the elimination is not base catalyzed but rather a palladium hydride elimination from a σ-allylic palladium intermediate present in equilibrium with the π-allylic complex probably occurs. One piece of evidence strongly supporting this mechanism of elimination is the fact that compounds XVI-Cl and XV-Cl once formed are relatively stable in triethylamine solution and this would not be expected if based-catalyzed elimination of palladium hydride was favorable. We cannot exclude the possibility of either the dienes or amine adducts being formed to a small extent by some other mechanism, but since stoichiometric and catalytic reactions give similar product mixtures in all cases, the π-allylic mechanism probably is the one operating. We have demonstrated also that complex I-Br with tri-*o*-tolylphosphine functions as a catalyst for the bromobenzene–isoprene–piperidine reaction and gives the same products in the same yields as the palladium acetate catalyst. Therefore, with the catalytic reactions we have studied, we believe that products are formed by the reaction paths shown in Scheme I.

Conclusions. We can conclude that both dienes and amine adducts are produced from the same π-allylic palladium complexes and that these complexes probably are the source of products in the catalytic diene phenylations we have studied. These reactions can be significantly influenced by the addition of ligands or other anions to the reaction mixtures. The nucleophilic attack of sec-

ondary amines upon π-allylic systems appears to be quite selective in unsymmetrical complexes. A primary allylic carbon is attacked in preference to a secondary one and an allylic carbon with *gem*-dimethyl substituents is preferred to a secondary allylic carbon. The catalytic reaction provides a convenient method for adding a functionalized four or more carbon atom chain to an aromatic ring.

Experimental Section

The analytical data, NMR spectra, and melting points of the π-allylic palladium complexes are given in Table III and the corresponding data for the amine reaction products are given in Table IV. (See note on supplementary material at the end of this paper.)

Materials. The palladium acetate and chloride used in this work were obtained from the Matthey Bishop Company. Acetonitrile (J. T. Baker) was dried with molecular sieves before use. Phenylmercuric chloride was used as received from Ventron. *m*-(Chloromercuri)benzaldehyde was obtained by our published procedure.[9] 2,4-Dimethoxyphenylmercuric chloride was obtained by mercurating resorcinol dimethyl ether in acetic acid with mercuric acetate and then adding aqueous calcium chloride. *n*-Butylmercuric chloride was obtained from the reaction of di-*n*-butylmercury (Pfaltz and Bauer) with mercuric chloride in methanol solution. (Carbomethoxy)mercuric chloride was prepared by the literature method.[10] The dienes were used as received from commercial sources (Matheson, Aldrich, or Chem Samples Co.). 1,3-Pentadiene (Aldrich) was fractionated before use to obtain mainly the *E* isomer. Methyl sorbate was prepared by esterification of the acid via the acid chloride. Methyl 5-methylsorbate was obtained by the literature method.[2] Piperidine (Aldrich), morpholine (Fisher), diisopropylethylamine (Aldrich), and triethylamine (Aldrich) were also used as received. Tri-*o*-tolylphosphine and tris(2,3,4,5-tetramethylphenyl)phosphine were prepared as described in the literature.[11] The other phosphines, triphenyl-, tris(*m*-chlorophenyl)-, and triethylphosphines and diphos, were used as received from Strem.

General Procedure for Preparation of π-Allylic Palladium Complexes. In a 250-mL Pyrex bottle was placed 100 mL of 0.10 M lithium chloropalladate solution in acetonitrile.[6] The diene was added (0.0125 mol) and the solution was stirred for 10 min. The organomercurial (0.010 mol) was then added with stirring in four portions over 45 min during which time the solution turned dark. After being stirred at room temperature for 24 h, the yellow solution was filtered through Celite 545 to remove suspended salts and palladium metal. Methylene chloride (200 mL) was added to the filtrate and the solution was washed with water (2 × 100 mL). After being dried ($MgSO_4$), the solvent was removed in vacuo and the residual oil was chromatographed on alumina (Fisher). Elution of the palladium complex occurred with 3% methanol in methylene chloride. The solvent was removed in vacuo at room temperature to yield a yellow oil. Crystallization was induced by several methods including (1) addition of ether and cooling, (2) addition of pentane to the ether solution and cooling, or (3) dissolution in hot hexane and cooling.

General Procedures for Reaction of π-Allylic Palladium Complexes with Amines. The second method below was used if Method A gave significant amounts of reduced dienes or if a phosphine or dipyridyl was added.

Method A. The amine (15 mmol) was placed in a heavy-walled Pyrex tube containing a magnetic stirring bar. The dimeric palladium complex (0.5 mmol) was added in portions at room temperature with stirring until it dissolved to form a yellow solution. The tube was capped with a rubber-lined one-holed metal cap and heated to 100 °C with stirring in a steam bath. As the reaction proceeded, palladium metal and the amine hydrohalide precipitated from the solution. The reactions were complete in about 1 h. After the mixture cooled, 1-methylnaphthalene (0.0355 g, 0.25 mmol) was added by syringe as an internal standard. Yields were determined by gas chromatographic analysis using predetermined sensitivity coefficients, and products were isolated by preparative-scale gas chromatography.

Method B. The palladium complex (0.5 mmol) was placed in a heavy-walled Pyrex tube containing a stirring bar. Acetonitrile (2 mL, 38 mmol) was added in one portion and the mixture was stirred for 5 min at room temperature. The phosphine (1.00 mmol) (0.50 mmol of diphos) was added (if desired) and the solution was stirred at room temperature for 5 min. (If the palladium complex was not completely soluble in acetonitrile, the addition of the phosphine effected dissolution.) The amine (2.5 mmol) was added and the tube was capped as above and heated to 100 °C with stirring in a steam bath. Palladium metal precipitated during the reaction. After 1 h, the reaction was allowed to cool, 1-methylnaphthalene (0.0355 g, 0.25 mmol) was added as an internal standard, and yields and products were determined as above.

General Procedure for Preparation of π-Allylic Palladium Iodides and Bromides. The π-allylic palladium acetate complex (5 mmol, prepared from the chloride by the method of Shaw[12]) was dissolved in 40 mL of methylene chloride at room temperature with stirring. The lithium halide (10 mmol) dissolved in 30 mL of acetone was added in one portion and the solution was stirred for 24 h at room temperature. As the reactions proceeded, lithium acetate came out of solution. After 24 h, the reaction mixture was poured into 200 mL of methylene chloride and the solution was washed with water (2 × 100 mL). The solution was dried over $MgSO_4$ and the solvent was removed in vacuo at room temperature to yield yellow-orange oils. Addition of ether and cooling (−5 °C) usually resulted in crystallization. Addition of pentane to the ether solution gave a second crop of crystals of the product.

General Procedure for Palladium-Catalyzed Reaction of Halobenzenes with Conjugated Dienes and Amines. These reactions were carried out by the method described previously.[1] An example appears below.

3-Methyl-1-phenyl-1,3-pentadiene and 3-Methyl-4-morpholino-1-phenyl-2-pentene. Palladium acetate (0.448 g, 2 mmol) and tri-*o*-tolylphosphine (1.216 g, 4 mmol) were placed in a heavy-walled Pyrex bottle. Bromobenzene (15.7 g, 100 mmol), (*Z*)-3 methyl-1,3-pentadiene (10.25 g, 125 mmol) and morpholine (21.78 g, 250 mmol) were added. The bottle was capped and the mixture was shaken until homogeneous. The reaction mixture was heated to 100 °C in a steam bath for 38 h at which time GLC analysis indicated that no halide remained. After the reaction mixture was cooled, it was diluted with ether and 10% aqueous NaOH. The products were extracted with (2 × 100 mL) ether. The ether extracts were dried over $MgSO_4$ and concentrated under reduced pressure at room temperature. Distillation of the residual oil through a short Vigreux column afforded 3-methyl-1-phenyl-1,3-pentadiene, bp 46–48 °C (0.6 mm)(8.69 g, 55 mmol), in 55% yield and 3-methyl-4-morpholino-1-phenyl-2-pentene, bp 133–135 °C (0.6 mm)(8.09 g, 33 mmol), in 33% yield.

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Registry No. I (X = Cl), 74312-65-5; I (X = Br), 74312-66-6; I (X = I), 74312-67-7; I (X = OAc), 74312-68-8; II, 74318-48-2; III, 74312-69-9; IV, 74312-70-2; V, 74312-71-3; VI, 74312-72-4; VII (X = Cl), 74312-73-5; VII (X = Br), 74312-74-6; VII (X = I), 74312-75-7; VII (X = OAc), 74312-76-8; VIII, 74312-77-9; IX, 74312-78-0; X, 74312-79-1; XI, 74312-80-4; XII, 41449-89-2; XIII, 41449-90-5; XIV, 67463-14-3; XV, 74318-49-3; XVI, 74312-81-5; XVII, 74312-82-6; isoprene, 78-79-5; (*E*)-1,3-pentadiene, 2004-70-8; 2,3-dimethyl-1,3-butadiene, 513-81-5; (*E*)-3-methyl-1,3-pentadiene, 2787-43-1; 4-methyl-1,3-pentadiene, 926-56-7; (*E,E*)-2,4-hexadiene, 5194-51-4; (*E,Z*)-2,4-hexadiene, 5194-50-3; methyl sorbate, 689-89-4; 2,4-dimethyl-1,3-pentadiene, 1000-86-8; 2,4-octadiene, 13643-08-8; methyl (*E*)-5-methyl-2,4-hexadienoate, 52148-91-1; piperidine, 110-89-4; morpholine, 110-91-8; bromobenzene, 108-86-1; 2-phenyloctadiene, 74312-87-1; methyl 5-methyl-2-phenyl-2,4-hexadienoate, 74312-50-8; (*E*)-$PhCH{=}CHC(CH_3){=}CH_2$, 68036-69-1; $PhCH_2CH{=}C(CH_3)_2$, 4489-84-3; $Ph(CH_2)_2CH(CH_3)_2$, 2049-94-7; (*E*)-$PhCH_2CH{=}C(CH_3)CH_2N(CH_2)_5$, 74312-51-9; (*E*)-$PhCH_2CH{=}C(CH_3)CH_2N(CH_2CH_2OCH_2CH_2)$, 74312-52-0; (*E*)-$PhCH{=}C(CH_3)C(CH_3){=}CH_2$, 30625-97-9; $PhCH_2C(CH_3){=}C(CH_3)CH_2N(CH_2)_5$, 74312-53-1; (*E*)-$PhCH{=}CHCH{=}C(CH_3)_2$, 39491-73-1; (*E*)-$PhCH_2CH{=}CHC(CH_3){=}CH_2$, 74312-54-2; (*E*)-$PhCH_2CH{=}CHC(CH_3)_2N(CH_2)_5$, 74312-55-3;

(12) S. D. Robinson and B. L. Shaw, *J. Organomet. Chem.*, 3, 367 (1965).

$Ph(CH_2)_3CH(CH_3)_2$, 4215-86-5; $Ph(CH_3)CHCH{=}CHC(CH_3)_2N(CH_2)_5$, 74312-56-4; $CH_3CH_2CH{=}C(CH_3)CH_2N(CH_2)_5$, 74312-57-5; $CH_2{=}C(CH_3)CH{=}CHCH_3$, 1118-58-7; $(CH_2)_5NCH_2C(CH_3){=}CHCH_2CH_3$, 74312-57-5; (*E,E*)-$PhCH{=}CHCH{=}CHCH_3$, 3909-96-4; (*E*)-$PhCH_2CH{=}CHCHN(CH_2CH_2OCH_2CH_2)CH_3$, 74318-47-1; (*E*)-$PhCH(CH_3)CH{=}CHCHN(CH_2)_5CH_3$, 74312-58-6; (*E,E*)-$PhC(CH_3){=}CHCH{=}CHCO_2CH_3$, 74312-59-7; $CH_3CH{=}CHC(Ph){=}CHCO_2CH_3$, 74312-60-0; (*E*)-$PhCH_2C(CH_3){=}CHC(CH_3){=}CH_2$, 74312-61-1; (*E*)-$PhCH{=}C(CH_3)CH{=}C(CH_3)_2$, 74312-62-2; $PhCH(CH_3)CH{=}CHCHN(CH_2)_5(CH_2)_5(CH_2)_2CH_3$, 74312-63-3; $PhCH(CH_3)CHN(CH_2)_5CH{=}CH(CH_2)_2CH_3$, 74312-64-4.

Supplementary Material Available: Table III listing the analyses, melting points, and NMR spectral data of the π-allylic palladium complexes prepared and Table IV giving the boiling points, exact masses, and NMR spectral data of the amine reaction products (6 pages). Ordering information is given on any current masthead page.

Reaction of Triarylphosphines with Tetramethyl-1,2-dioxetane: Kinetics of Formation and Decomposition of 2,2-Dihydro-4,4,5,5-tetramethyl-2,2,2-triaryl-1,3,2-dioxaphospholanes

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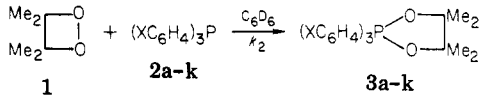
The reaction of a series of triarylphosphines $[(XC_6H_4)_3P]$ with tetramethyl-1,2-dioxetane (1) in C_6D_6 produced a series of 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triaryl-1,3,2-dioxaphospholanes in high yield. Thermal decomposition of the phosphoranes produced tetramethylethylene oxide and the corresponding triarylphosphine oxides in all cases. The kinetics of phosphorane formation and decomposition in benzene was investigated. The rate data for phosphorane formation showed a reasonable correlation with σ^+ constants (correlation coefficient $\sim$0.98: $\rho = -0.82$). The results are not consistent with nucleophilic attack on oxygen by phosphorus but rather with a concerted (biphilic) insertion into the peroxy bond of the dioxetane. Phosphorane decomposition (at 38 °C) was found to be substantially more sensitive to substituent effects than phosphorane formation. A good correlation of phosphorane decomposition with Hammett σ constants was obtained (correlation coefficient = 0.997, $\rho = -3.51 \pm 0.24$). This result is consistent with a mechanism that involves heterolytic cleavage of a phosphorus–oxygen bond followed by the irreversible internal displacement of triarylphosphine oxide.

1,2-Dioxetanes have been shown to undergo a characteristic chemiluminescent thermal decomposition to two carbonyl fragments.[2] Dioxetanes also undergo a number of interesting reactions in which no excited products are formed. Metal ions have been shown to catalytically decompose dioxetanes to carbonyls via a dark pathway.[3] Tetramethyl-1,2-dioxetane has been shown[4] to undergo rearrangement, upon treatment with boron trifluoride, to yield products characteristic of the involvement of a carbonyl oxide intermediate. Insertion into the peroxy bond of 1,2-dioxetanes by various reagents has been shown to produce phosphoranes[5] and sulfuranes,[6] as well as arsenic(V) and antimony(V) compounds.[7] The reaction with trivalent phosphorus compounds is a synthetically useful method for the preparation of phosphoranes.[5b,c] The reaction of triphenylphosphine with tetramethyl-1,2-dioxetane was shown[5a] to produce a stable phosphorane which underwent characteristic thermal decomposition, the net effect of which was the deoxygenation of the dioxetane to the epoxide. Triphenylphosphine has been employed[5d,8] in similar reaction sequences to characterize dioxetanes. Other than an initial report,[5b] little is known about the mechanism of insertion into the peroxy bond of dioxetanes by trivalent phosphorus compounds. In the present study, we report the kinetics of formation of a series of phosphoranes produced by the reaction of triarylphosphines $[(XC_6H_4)_3P]$ with tetramethyl-1,2-dioxetane, as well as the kinetics of decomposition of several of the phosphoranes.

Results

The reaction of tetramethyl-1,2-dioxetane (1) with triarylphosphines (**2a–k**) in C_6D_6 at low temperature produced 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triaryl-1,3,2-dioxaphospholanes (**3a-k**) in yields of generally 90% or higher (Table I; reaction 1). As previously noted[5a] for **3e**,



1 **2a-k** **3a-k**

the major side product in all of the reactions was pinacolone with concomitant formation of phosphine oxide. 2,3-Dimethyl-3-hydroxybut-1-ene was noted as a minor side product in several cases. The side products were not due to decomposition of the phosphoranes but were di-

(1) ACS–PRF Catalyst-Project SEED participant, summer 1978.

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