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Palladium-Catalyzed Syntheses of Aryl Polyenes

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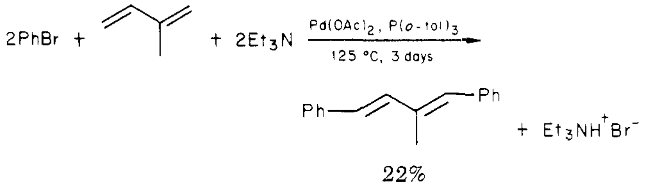
The palladium-catalyzed arylation reaction has been employed to prepare a variety of mono- and diaryl 1,3-dienes and 1,3,5-trienes. The yields were good when electron-withdrawing substituents were present in the aryl groups but only poor to fair when electron-donating groups were involved. Monoaryl dienes and trienes reacted well with all types of aryl halides to give mixed diaryl derivatives. 2-Bromostyrene reacts with phenylhexatriene to form 1,8-diphenyloctatetraene and with hexatriene to form 1,10-diphenyldecapentaene, but both only in about 15% yield.

The increasing interest in semiconducting organic molecules[1] for electronic applications has prompted us to examine the palladium-catalyzed arylation of alkenes as a new method for preparing possibly semiconducting aryl polyenes. We have previously reported the mono-[2] and diarylation[3] of isoprene with iodo- or bromobenzene, triethylamine, and a palladium acetate–tri-*o*-tolylphosphine catalyst. The yield of diarylated product was only 22% on the basis of the starting bromobenzene. However, only 50% of the bromide reacted. We now report a more detailed study of this type of reaction, including an investigation of its scope and applicability to the synthesis of a variety of arylated polyenes.

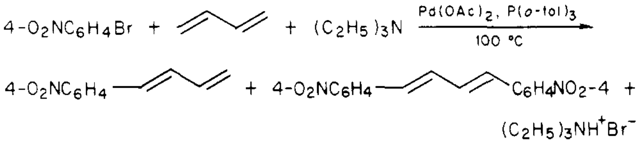


Results and Discussion

Conjugated Dienes. Seven conjugated dienes, 1,3-butadiene, isoprene, (*E*)-1,3-pentadiene, (*E*)-phenyl-1,3-butadiene, (*E* and *Z*)-1-*p*-anisyl-1,3-butadiene, and (*E*)-1-(*p*-nitrophenyl)-1,3-butadiene, were reacted with a variety of substituted aryl bromides and iodides by employing triethylamine as the base and palladium acetate–tri-*o*-tolylphosphine as catalyst. The reactions were carried out in capped bottles at 75–125 °C. In all examples, products were mainly or only the trans mono- and diarylated 1,3-butadienes. The results are summarized in Table I.

Inspection of the data in Table I reveals a substantial substituent effect upon the arylation. The electron-withdrawing *p*-nitro, acetyl, carbomethoxy and cyano groups enhanced the rates of arylation and improved the yields of 1,4-diaryl-1,3-butadienes obtained compared with the unsubstituted phenyl compound. The rates of reaction of bromobenzene, *p*-bromotoluene, and *p*-bromoanisole, on the other hand, were so low that we generally employed 10 mole % palladium acetate with 20 mole % tri-*o*-tolylphosphine as catalyst rather than the usual 1 or 2 mole % to complete the reactions in a reasonable time. Not only were the rates of reaction of the aryl bromides with para electron-donating groups low, the reactions generally stopped before the aryl halides were completely consumed. In these cases, the rate of polymerization of the butadiene is faster than the arylation even with 10% catalyst so that the yields of mono- and diarylbutadienes are less than 50% of the theoretical yield.

It is clear from the reaction of iodobenzene with butadiene, that 1-phenyl-1,3-butadiene is more easily arylated than butadiene is since phenylbutadiene, a necessary intermediate, does not accumulate. Even using a 2.5 to 1.0 ratio of butadine to iodobenzene only resulted in the formation of 24% 1-phenylbutadiene along with 34% of the diphenyl diene. A similar result was obtained in the reaction of *p*-bromonitrobenzene with butadiene. With a 2:1 ratio of butadiene to the nitrobromide, 17% mono- and 27% diarylated products were obtained while with a 5:1 ratio, 46% mono- and 12% diaryl products were formed.



As observed in other arylation reactions, iodobenzene is more reactive (~5 times) than bromobenzene is with butadiene.

Attempts to selectively form unsymmetrically substituted 1,4-diarylbutadienes in a single reaction from butadiene and two different aryl halides were unsuccessful. A near statistical distribution of the three possible products was obtained from a mixture of *p*-iodonitrobenzene and methyl *p*-iodobenzoate. A very low yield of a mixture of arylated dienes was formed from *p*-bromotoluene and *p*-bromoanisole. They reacted very slowly with butadiene and gave little of the unsymmetrical diarylated diene. Isolation of the monoaryl diene followed by a second arylation does work well, however, to form the unsymmetrical dienes (see below).

Attempts to arylate butadiene at 100 °C with *p*-bromophenol or *p*-bromoaniline were unsuccessful and only intractable dark solids were formed.

Isoprene is a little less reactive than butadiene, and, as expected, monoarylation is much preferred over diarylation since the disubstituted, second double bond is much less reactive than the first one. We have not been able to find conditions where more than about 30% yields of diarylated products are formed. Again the problem appears to be that the isoprene and monoarylisoprenes undergo polymerization and Diels–Alder-type reactions competitively with the arylation. *p*-Bromonitrobenzene, for example, with a 2:1

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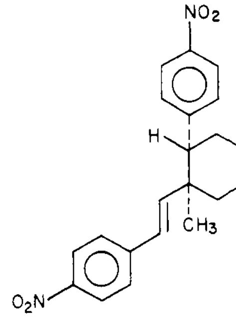
[1] For example, see: *Chem. Eng. News* 1982, April 19, *60*, 29.

[2] Patel, B. A.; Dickerson, J. E.; Heck, R. F. *J. Org. Chem.* 1978, *43*, 5018.

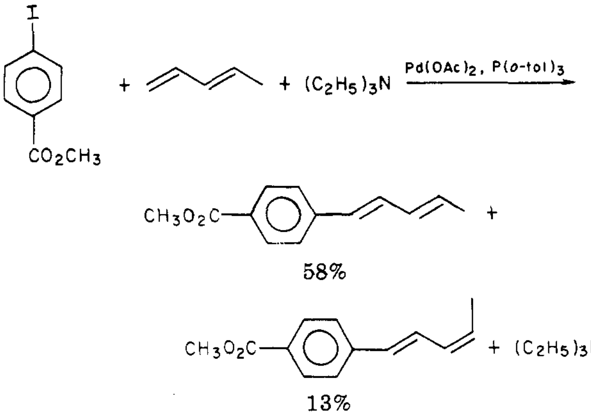
[3] Fischetti, W.; Mak, K. T.; Stakem, F. G.; Kim, J.-I.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* 1983, *48*, 948.

ratio of bromide to isoprene and 1 % catalyst at 100 °C in 72 h gave 27% monoaryl diene, 10% diaryl diene, and 10% of a Diels–Alder adduct of the diarylated product with isoprene. The structure of the Diels–Alder product was determined by X-ray crystallography by Dr. Arnold Rheingold of these laboratories.[17] Surprisingly, the methyl-substituted double bond of the (*E,E*)-diaryl diene reacted with the isoprene. We have no explanation for why the more substituted double bond reacted. The structure of the product is shown below. Crystallographic data are given in the supplementary material section (see note at the end of this paper)

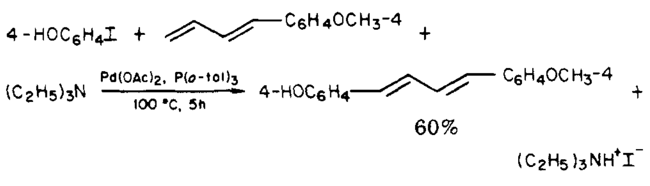


In all isoprene reactions, substituents in the aryl halide influence the reaction similarly to the way they did in the butadiene examples. Monsubstitution occurs only at the monosubstituted isoprene double bond, and the products are, at least, mainly the *E* or *E,E* isomers. In the case of iodobenzene, the diphenyl diene (32%) is a 1:3 mixture of the *Z,E* and *E,E* isomers.

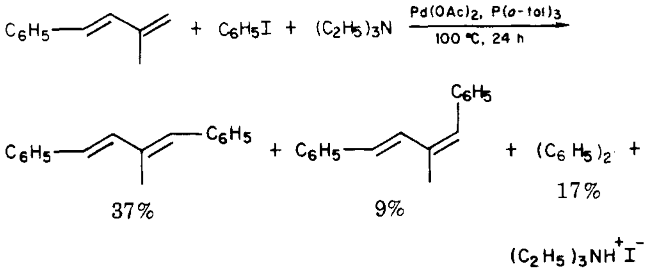
(*E*)-1,3-Pentadiene is similar to isoprene, but it is even more difficult to obtain diarylated products from it and significant amounts of *Z* isomers are formed in some reactions. For example, methyl *p*-iodobenzoate and (*E*)-1,3-pentadiene with 8% catalyst at 100 °C for 15 h gave a 71% yield of an 80:20 mixture of *E,E*:*E,Z* isomers of the monoarylated diene.



Several monoarylated dienes were submitted to a second arylation. Good yields were obtained from the 1-phenyl-, 1-*p*-anisyl-, and 1-(*p*-nitrophenyl)-1,3-butadienes even with aryl halides with strongly electron-donating para substituents. For example, 1-*p*-anisyl-1,3-butadiene gave about the same yields of unsymmetrical diarylated dienes with *p*-bromophenol (~60%) as it did with *p*-iodoanisole and methyl *p*-iodobenzoate. Similarly, 1-(*p*-nitrophenyl)-1,3-butadiene and *p*-bromoaniline gave the expected diarylated diene in 79% yield.



Phenylation of phenylisoprene with iodobenzene was slow even with 10% catalyst, but the yield of the diphenylisoprene (*E,E* and *E,Z*) was about 14% better (46%) than that obtained in one step from isoprene. Also formed was 17% biphenyl.



Attempted reaction of *p*-iodonitrobenzene with 1-(*p*-carbomethoxyphenyl)-1,3-pentadiene gave only a 71% conversion of the iodide in 24 h with 10% catalyst, and the only product we could isolate was *p,p'*-dinitrobiphenyl in 29% yield.

The results obtained in the arylation of 1,3-dienes are understandable on the basis of the usual mechanism proposed previously for these reactions.[4] The suggested mechanism is shown in Scheme I with 1,3-butadiene as the diene.

Elimination of $HPdL_2X$ probably occurs from the σ-allylic palladium intermediates, which are in equilibrium with one or more isomeric π-allylic forms. This process equilibrates isomers and may lead to isomeric mixtures of dienes in the final elimination. The elimination is probably base (amine) catalyzed as observed with (carbomethoxymethyl)(π-allyl)palladium chloride.[5] We can explain the low rates of reaction of the aryl halides with electron-donating groups as due to the low acidity of benzylic or allylic hydrogens in the σ-allylic intermediates. The low acidity retards the rate of the base-catalyzed elimination and the recycle of the palladium. Once the first aryl group is added to the diene, and if there are no steric problems with the addition of the second aryl group, the diarylated σ-allylic palladium intermediates are formed and they are sufficiently activated (acidified) by the two aryl groups that elimination is now facile. In the cases where recycle of the palladium is slow, polymerization and Diels–Alder and perhaps oligomerization reactions of the dienes occur competitively and may consume the diene before the halide has all reacted. The slow rates of diarylation of isoprene and 1,3-pentadiene are probably due to steric factors which greatly slow down the addition of the second aryl group, and, therefore, the polymerization, etc., of the monoaryl dienes and/or the self coupling of the aryl halides become the dominant reactions.

We have noted in carrying out many diene arylations with the palladium acetate–tri-*o*-tolylphosphine catalyst that the reaction begins homogeneously, but soon orange to red crystals appear in the solution. Continued heating causes these to slowly redissolve and the arylation proceeds. We have separated the crystals and find that they are halogen-bridged dimeric cyclopalladated products with palladation occurring on an ortho methyl of the *o*-tolyl groups in the phosphine. The structure of the iodide complex was established by X-ray crystallography, the details of which will be published elsewhere.[6] The com-

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[4] Dieck, H. A.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083.

[5] Larock, R. C.; Mitchell, M. A. *J. Am. Chem. Soc.* **1976**, *98*, 6718.

[6] Fultz, W.; Rheingold, A., to be published.

Table I. Arylation of 1,3-Dienes[a]

diene	halide	diene/halide	Pd(OAc)$_2$,[b] mol %	time,[c] h	% conversion of halide	% yield of products[d]	
						1-aryl 1,3-diene	1,4-diaryl 1,3-diene
$CH_2=CHCH=CH_2$	C_6H_5I	0.5	2.5	70	80	6[e]	29
	C_6H_5I	0.5	5	48	95	4[e]	38
	C_6H_5I	0.5	10	17	98	2[e]	43
	C_6H_5I	2.5	10	16	100	24[e]	34
	C_6H_5Br	0.5	10	126	88	7[e]	32
	p-$CH_3C_6H_4I$	0.5	10	48	100		48
	p-$CH_3OC_6H_4I$	0.5	1	72 (48, 125 °C)			15
	p-$CH_3OC_6H_4I$	2	10	24	100	10	20
	p-$CH_3OC_6H_4I$	0.5	10	23	100	21[e]	28
	p-NCC_6H_4Br	0.5	2	72	90		65
	p-$O_2NC_6H_5Br$	0.5	1	24	100		69
	p-$O_2NC_6H_5Br$	2	1	24	100	17	27
	p-$O_2NC_6H_5Br$	5	1	2	100	46	12
	p-$CH_3COC_6H_4Br$	0.5	1	36	100		72
	p-$CH_3O_2CC_6H_4I$	0.55	1	24	100		75
	p-$O_2NC_6H_4I$ p-$CH_3O_2CC_6H_4I$	0.55[g]	2	24	100		p-$O_2NC_6H_4(CH=CH)_2C_6H_4NO_2$-$p$ (19)[f] p-$O_2NC_6H_4(CH=CH)_2C_6H_4CO_2CH_3$ (29)[f] p-$CH_3O_2CC_6H_4(CH=CH)_2C_6H_4CO_2CH_3$ (16)[f]
	p-$CH_3C_6H_4Br$ p-$CH_3OC_6H_4Br$	0.55[g]	2	120	45, 43[h]		p-$CH_3C_6H_4(CH=CH)_2C_6H_4CH_3$-$p$ (3)[f] p-$CH_3C_6H_4(CH=CH)_2C_6H_4OCH_3$ (5)[f] p-$CH_3OC_6H_4(CH=CH)_2C_6H_4OCH_3$ (3)[f]
$CH_2=C(CH_3)CH=CH_2$	C_6H_5I	2	1	48 (72 at 125 °C)	80	9	
	C_6H_5I	2	10	96	96	40	4[e]
	C_6H_5I	0.5	10	24	95	31[e]	32 (E/Z = 3)[e]
	C_6H_5Br	0.5	1	72 at 125 °C			22
	p-$CH_3OC_6H_4I$	0.5	1	96 at 125 °C	60		12
	p-$CH_3OC_6H_4I$	0.5	10	19	100	27[e]	31
	p-$CH_3OC_6H_4I$	2	10	38	100	32	
	p-$O_2NC_6H_4Br$	2	1	72		27	10[i]
	p-$O_2NC_6H_4Br$	0.5	2	72 (39 at 125 °C)			20
	p-$CH_3O_2CC_6H_4Br$	2	10	46	90	16	5
(E)-$CH_2=CHCH=CHCH_3$	C_6H_5I	1.5	5	23	100	74 (E/Z = 4)	
	C_6H_5I	0.5	10	20	100	51	7
	p-$CH_3OC_6H_4I$	0.5	1[j]	24		29	
	p-$O_2NC_6H_4Br$	2	1	39	100	66	
	p-$CH_3O_2CC_6H_4I$	1.2	8	15	100	71 (E/Z = 4)	
(E)-$C_6H_5CH=CHCH=CH_2$	p-$CH_3OC_6H_4I$	1	2	4			66
	p-$O_2NC_6H_4Br$	1	2	5	100		82
	p-$CH_3O_2CC_6H_4Br$	1	2	6	95		72
(E and Z)-p-$CH_3OC_6H_4CH=CHCH=CH_2$	p-HOC_6H_4Br	1[k]	2	23 at 75 °C	100		60
	p-$CH_3OC_6H_4Br$	1	2	5	100		65
	p-$CH_3O_2CC_6H_4I$	1	2	2	100		61
(E)-p-$O_2NC_6H_4CH=CHCH=CH_2$	p-$H_2NC_6H_4Br$	1	2	24 at 70 °C	100		79

(*E*)-$C_6H_5CH{=}CHC(CH_3){=}CH_2$	C_6H_5I	1^{l}	10	24			46 (*E*/*Z* = 4)^{m}
(*E*,*E*)-$CH_3O_2CC_6H_4CH{=}CHCH{=}CHCH_3$	*p*-$O_2NC_6H_4I$	0.67^{n}	10	24	71	([4-$O_2NC_6H_4$]$_2$ 29]	

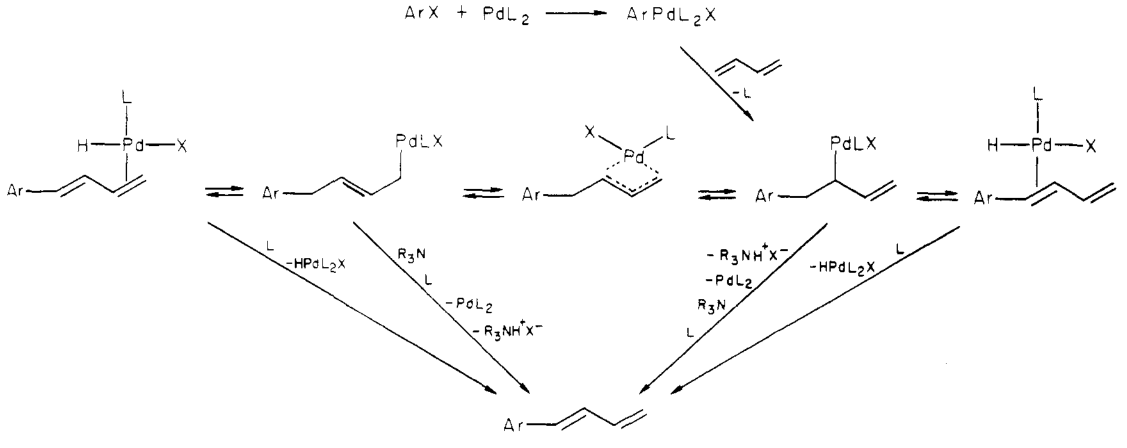
[a] Unless otherwise noted, 3 molar equiv of triethylamine were added per mol of aryl halide. [b] Unless noted, 2 molar equiv of tri-*o*-tolylphosphine were employed per mol of palladium acetate. [c] Reaction time at 100 °C unless noted otherwise. [d] Yields of isolated products except where noted. [e] Yields determined by GLC. [f] Yield determined by HPLC. [g] Molar ratio of the diene to a 1:1 molar mixture of the two halides. [h] Conversion of the *p*-bromoanisole. [i] A 10% yield of a Diels–Alder adduct of isoprene with the 1,4-bis(*p*-nitrophenyl)isoprene was also obtained. [j] A 1:4 molar ratio of palladium acetate to tri-*o*-tolylphosphine was used. [k] 5 molar equiv of triethylamine were employed relative to the halide. [l] 30 molar equiv of triethylamine were used. [m] Also, 17% biphenyl was detected. [n] 8 molar equiv of triethylamine were used.

Table II. Arylation of Conjugated Trienes[a]

triene	halide	triene/halide	$Pd(OAc)_2$,[b] mol %	time,[c] h	% conversion of halide	% yield of 1,6-diaryl triene[d]
$CH_2{=}CHCH{=}CHCH{=}CH_2$	C_6H_5I	0.5	10	6	100	18
	p-HOC_6H_4Br	0.5	4	14 at 75 °C	100	5
	p-$AcOC_6H_4Br$	0.5^{e}	4	120 at 75 °C	80	30
	p-$CH_3OC_6H_4I$	0.5	10	6	100	6
		0.5	10	20 at 75 °C	100	6
	p-$O_2NC_6H_4Br$	0.5	1	72	95	65
		5.0^{f}	5	1	100	20, 54^{g}
	o-$O_2NC_6H_4Br$	0.5	2	15 at 75 °C	100	54
	p-$CH_3O_2CC_6H_4I$	0.4^{h}	5	4	67	30
	p-$CH_3O_2CC_6H_4Br$	0.5	2	39 at 75 °C	78	54
	m-$CH_3O_2CC_6H_4Br$	0.5	2	137 at 75 °C	60	37
	p-$CH_3COC_6H_4Br$	0.5	5	1	100	63
	p-$OCHC_6H_4Br$	0.5	2	20 at 75 °C	100	89
	(*E*)-$C_6H_5CH{=}CHBr$	0.5^{i}	10	19	100	14% 1,10-diphenyldecapentaene
	(*E*)-*p*-$CH_3OC_6H_4CH{=}CHBr$	0.5^{i}	10	20 at 75 °C	100	15% 1,10-di-*p*-anisyldecapentaene
$CH_2{=}CHCH{=}CHCH{=}CHCH_3$	*p*-$CH_3O_2CC_6H_4I$	0.5	2	28	100	25
$C_6H_5(CH{=}CH)_2CH{=}CH_2$	*p*-$CH_3OC_6H_4I$	1	2	4	90	55
	p-$O_2NC_6H_4Br^{j}$	1	2	20	98	56
	p-$CH_3O_2CC_6H_4Br^{j}$	1	2	19	100	55
	p-$C_6H_4I_2{}^{e}$	2	2	17	100	11% of *p*-bis(phenylhexatrienyl)benzene
	(*E*)-$C_6H_5CH{=}CHBr^{i}$	1	2	17	95	16% of 1,8-diphenyloctatetraene
4-$O_2NC_6H_4(CH{=}CH)_2CH{=}CH_2$	*p*-$H_2NC_6H_4Br$	0.8	5	12		56% 1-(4-nitrophenyl)-6-(4-aminophenyl)-1,3,6-hexatriene

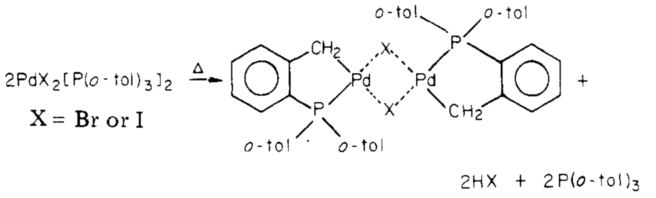
[a] Unless otherwise noted, 3 molar equiv of triethylamine were added per mol of halide. [b] 2 mol of tri-*o*-tolylphosphine were added per mol of palladium acetate. [c] Reaction time at 100 °C except where noted. [d] Yields of isolated products. [e] 12 mol of triethylamine were used per mol of halide. [f] 5 mL of acetonitrile were used as solvent and 5 mol % of *N*-phenyl-2-naphthylamine was added as a polymerization inhibitor. [g] Yield of 1-(*p*-nitrophenyl)-1,3,5-hexatriene. [h] 4.8 mol of triethylamine per mol of halide were used. [i] 0.5 mL of hexamethylphosphoramide was added per mmol of halide. [j] 6 mol of triethylamine were used per mol of halide.

Scheme I[a]



[a] L = $P(o\text{-tol})_3$; X = Br or I.

plexes obtained from aryl iodide reactions appear by NMR to be similar to the ones obtained from aryl bromides.



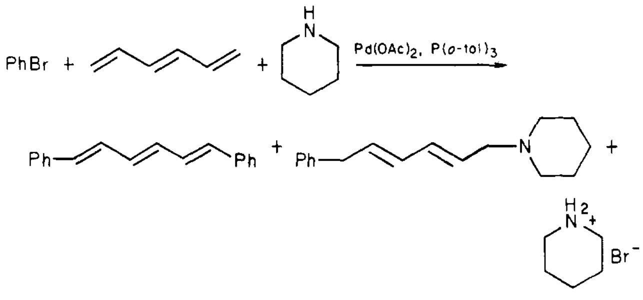
Analogous compounds have been reported.[7] It is significant that the pure cyclometalated iodide complex is *not* a catalyst for the diene arylation unless some triethylammonium iodide also is added. Presumably, the amine salt is able to convert the cyclopalladated complex back into the catalytically active simple bis(phosphine) complex.

Conjugated Trienes. Four conjugated trienes, 1,3,5-hexatriene, 1,3,5-heptatriene, 1-phenyl-1,3,5-hexatriene, and 1-(*p*-nitrophenyl)-1,3,5-hexatriene, were arylated with a variety of aryl halides. The results are summarized in Table II.

The 1,3,5-hexatriene used was about 69% trans. Both 1,3,5-heptatriene and 1-phenyl-1,3,5-hexatriene were mixtures of stereoisomers. The 1-(nitrophenyl)-1,3,5-hexatriene was the *E,E* isomer. The products obtained in all cases were essentially only the all-trans isomers, presumably because equilibration occurred under the reaction conditions.

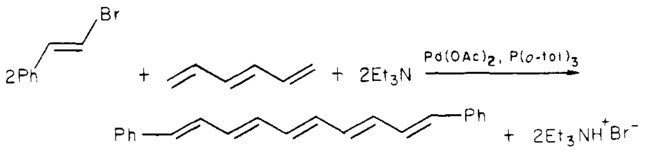
We did not find significant amounts of monoarylhexatrienes in the 2:1 aryl halide–triene reactions, but these products could be favored as in the diene case by employing a large exess of hexatriene. Thus, *p*-nitrobromobenzene with 5 mol of hexatriene gave 10% diaryl and 54% monoaryl triene.

We briefly examined the arylation of hexatriene in the presence of piperidine to determine if the monoarylpiperidinohexadienes could be obtained in good yields since these products should provide another route to the monoaryl trienes via the Hoffmann elimination. The reaction of bromobenzene, hexatriene, and piperidine was rather slow, and it produced the terminal piperidine adduct, but only in 30% yield along with 5% of the diphenylhexatriene. It is interesting that the terminal piperidine adduct was obtained. An S_N2' attack of piperidine upon the intermediate π-allylic complex may be involved. A similar reaction with *p*-bromoacetophenone and hexatriene with piperidine gave only about 40% of the crude piperidine adduct. Since the yields of piperidine adducts were not high in these examples, we prefer to use the one-step monoarylation procedure with triethylamine and excess hexatriene to prepare the 1-aryl-1,3,5-hexatrienes.



Substituent effects in the hexatriene diarylation are larger than those observed with butadiene. Thus, iodobenzene and *p*-iodoanisole with hexatriene gave less than 20% of the diarylhexatriene derivatives under conditions where butadiene gave nearly 50%. *p*-Bromophenyl acetate at 75 °C did slightly better and gave 30% diarylation. Better yields with much slower reactions were usually obtained at 75 °C than at 100 °C,[8] particularly with hexatriene. Electron-withdrawing substituents generally improved the reaction. Methyl *p*-bromobenzoate, *p*-bromonitrobenzene, *p*-bromoacetophenone, and *p*-bromobenzaldehyde gave 54–89% of the diaryl derivatives. *o*-Bromonitrobenzene also reacted well, giving 54% of (*E*,*E*,*E*)-1,6-bis(*o*-nitrophenyl)-1,3,5-hexatriene. One meta derivative, methyl *m*-bromobenzoate, was reacted also (at 75 °C). The diarylated product was formed in 37% yield, but the conversion of the halide was only 60%.

Hexatriene reacted with (*E*)-2-bromostyrene to form 1,10-diphenyldecapentaene, but the yield was only 14%. Hexamethylphosphoramide was used as a solvent in the β-bromostyrene reactions since it gave somewhat better yields than were obtained without a solvent. *p*-Methoxy-2-bromostyrene reacted similarly at 75 °C to give 15% of the di-*p*-anisyldecapentaene.



The reaction of 1,3,5-heptatriene with methyl *p*-iodobenzoate took an unexpected course and gave as the only

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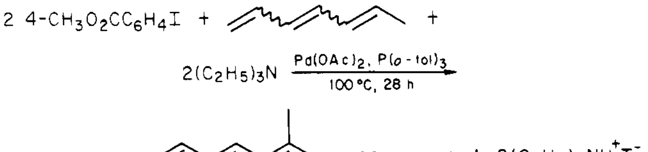
[7] Cheney, A. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 860.

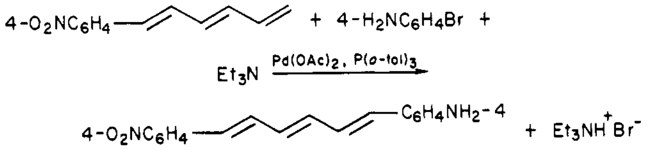
[8] Ziegler, C. B., Jr.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2941.

separable product the 1,6-diarylated triene in 25% yield. Unlike 1,3-pentadiene, diarylation occurred easily with 1,3,5-heptatriene. Why the triene reacts better is not clear.



Steric differences do not seem significant enough to produce the large difference in products observed.

1-Phenyl-1,3,5-hexatriene, like 1-phenylbutadiene, reacted reasonably well with methyl *p*-bromobenzoate, *p*-bromonitrobenzene, and *p*-iodoanisole, giving ca. 55% yields of diaryl derivatives in each case. A reaction of phenylhexatriene with *p*-diiodobenzene gave the expected bis(*p*-(phenylhexatrienyl))benzene, but only in 11% yield. The addition of 2-bromostyrene to phenylhexatriene, also, went poorly, giving only 16% of 1,8-diphenyloctatetraene. 1-(*p*-Nitrophenyl)hexatriene reacted moderately well with *p*-bromoaniline, giving the mixed diaryltriene in 56% yield.



Conclusions

1,3-Butadiene may be diarylated easily with aryl bromides or iodides possessing electron-withdrawing para substituents. Monoarylated dienes may be obtained if a large excess (5×) of butadiene over the halide is employed. Aryl halides with electron-donating substituents give low yields of diarylated products even with 10% catalyst. These compounds with electron-donating substituents often are probably better synthesized by a double Stobbe condensation.[9]

Monoarylation of isoprene and 1,3-pentadiene occurs moderately well, but diarylation is difficult. Unsymmetrical diaryl-1,3-butadienes are easily obtained from 1-aryl-1,3-butadienes and aryl bromides or iodides.

1,3,5-Hexatriene is similar to butadiene. It easily diarylates with aryl bromides or iodides with electron-withdrawing groups, and monoarylation is practical only with a large excess of hexatriene. Other diarylhexatrienes may be better prepared by Wittig reactions.[10] α,ω-Diaryl tetraenes and pentaenes have been made from trienes and 2-bromostyrene and its *p*-methoxy derivative but only in low yields. These methods may be the most convenient ones to use, however, depending upon the substituents desired. The arylation reaction tolerates a wider range of substituents that either of the alternative reactions, the Wittig or Stobbe reactions.

Experimental Section

Reagents. Most of the reagents used in this study were from commercial sources and were used without further purification. Exceptions were (*E*)-1-phenyl-1,3-butadiene,[11] (*E* and *Z*)-1-*p*-anisyl-1,3-butadiene,[12] (*E*)-2-methyl-4-phenyl-1,3-butadiene,[13] (*E* and *Z*)-1,3,5-hexatriene,[14] 1,3,5-heptatriene,[15] 1-phenyl-1,3,5-hexatriene,[12] and (*E*)-1-*p*-anisyl-2-bromoethylene,[16] which were prepared by published methods. The preparations of (*E*)-1-(*p*-nitrophenyl)-1,3-butadiene, (*E*,*E*)-1-(*p*-nitrophenyl)-1,3,5-hexatriene, and (*E*,*E* and *E*,*Z*)-1-(*p*-carbomethoxyphenyl)-1,3-pentadiene are given below.

General Procedure for the Arylation of Dienes and Trienes. In a thick-walled 200-mL Pyrex bottle were placed 0.0448 g (0.2 mmol) of palladium acetate, 0.121 g (0.4 mmol) of tri-*o*-tolylphosphine, 20 mmol of the aryl halide, 10 mmol of the diene or triene (or other amount as shown in Tables I or II), and 6.0 mL of triethylamine. In reactions with 1,3-butadiene the reaction mixture is cooled in a dry ice–acetone bath, the liquified diene is added, and the bottle is capped. Less volatile dienes and trienes were added at room temperature, and the bottles were flushed with nitrogen before they were capped. The solutions then were shaken with warming until the catalyst had dissolved and then they were heated at 75–125 °C in an oil bath or for 100 °C in a steam bath. Reactions at 75 °C were generally stirred magnetically while at higher temperatures the solutions were not stirred. When the reactions were complete or stopped as determined by GLC analyses of the aryl halide remaining in a sample of the reaction mixture, they were cooled and diluted with 80 mL of chloroform. The insoluble portion, if any, was rinsed with another 80 mL of chloroform. Many of the diaryl dienes and trienes were essentially insoluble in cold chloroform and could be purified by recrystallization with hot filtration through Celite from DMF or Me_2SO solutions. (Ether and water or aqueous acid also may be used instead of chloroform; see examples below.) If the product was soluble in chloroform, the solution was extracted with 1 N hydrochloric acid (only water was used in the preparation of the monoaryl dienes and trienes) to remove excess amine and amine salts. After the solution was washed with water and dried ($MgSO_4$), the solvent was removed under reduced pressure and the products were purified either by recrystallization, distillation, or chromatography. The properties of the products prepared are given in Table III in the supplementary material section.

Several examples of the general procedure follow.

(*E*,*E*)-1,4-Bis(*p*-nitrophenyl)-1,3-butadiene. In a 200-mL Pyrex bottle was placed 7.92 g (40 mmol) of 1-bromo-4-nitrobenzene, 0.090 g (0.4 mmol) of palladium acetate, 0.243 g (0.80 mmol) of tri-*o*-tolylphosphine, and 12 g (120 mmol) of triethylamine. The mixture was cooled in a dry ice–acetone bath and 1.08 g (20 mmol) of cold liquid butadiene was added. The bottle was immediately capped, shaken, and heated at 100 °C in a steam bath for 24 h behind a safety shield. After cooling, the bottle was opened, 100 mL of 5% hydrochloric acid and 100 mL of ether were added and the mixture was shaken. The product remained insoluble as large brown needle-like crystals and was separated by filtration. Recrystallization from hot Me_2SO (Celite) gave 3.6 g (69%) of long yellow needles of the product, mp 263–265 °C.

(*E*,*E*,*E*)-1,6-Bis(*p*-acetoxyphenyl)-1,3,5-hexatriene. A solution of 2.15 g (10 mmol) of *p*-bromophenyl acetate, 0.40 g (5 mmol) of 1,3,5-hexatriene, 0.090 g (0.40 mmol) of palladium acetate, 0.243 g (0.80 mmol) of tri-*o*-tolylphosphine, and 12 g (120 mmol) of triethylamine in a nitrogen-flushed Pyrex bottle was stirred magnetically at 75 °C for 5 days. After cooling, the bottle was opened, 80 mL of water and 80 mL of ether were added, and the product was separated by filtration. Recrystallization from hot xylene gave 0.52 g (30%) of yellow crystals of the triene, mp 225–227 °C.

The acetate (0.209 g, 0.6 mmol) was hydrolyzed with potassium hydroxide (0.67 g, 12 mmol) in 12 mL of methanol at room temperature under nitrogen for 1.5 h. Hydrochloric acid (6 mL of 6 N) was added at 0 °C to the reaction mixture. Pale yellow crystals of the phenol separated. These were recrystallized from methanol to give 0.101 g (68%) of the pure diphenol, 1,6-bis(*p*-hydroxyphenyl)-1,3,5-hexatriene, mp 273–274 °C.

(*E*)-1-(*p*-Nitrophenyl)-1,3-butadiene. A solution of 2.02 g (10 mmol) of *p*-bromonitrobenzene, 2.70 g (50 mmol) of butadiene,

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6.06 g of triethylamine, 0.0224 g (0.1 mmol) of palladium acetate, and 0.060 g (0.2 mmol) of tri-*o*-tolylphosphine prepared in a Pyrex bottle as in the preparation of the 1,4-bis(*p*-nitrophenyl)-1,3-butadiene above was heated at 100 °C in a steam bath for 2 h. The mixture was cooled, diluted with 50 mL of water, and 50 mL of ether, and the yellow crystals of the 1,4-bis(*p*-nitrophenyl)-1,3-butadiene present were separated by filtration and recrystallized from Me_2SO. There was obtained 0.37 g (24%) of this material. The ether layer of the filtrate was separated and washed with water and aqueous sodium bicarbonate. After drying ($MgSO_4$), the solvent was removed under reduced pressure and the residue was crystallized from methanol by cooling to −70 °C. There was obtained 0.80 g (46%) of long yellow needles of the mono(*p*-nitrophenyl)butadiene, mp 73–74 °C.

(*E,E*)-1-(*p*-Nitrophenyl)-1,3,5-hexatriene. In a 200-mL Pyrex bottle was placed 2.02 g (10 mmol) of *p*-bromonitrobenzene, 4.00 g (50 mmol) of 1,3,5-hexatriene, 3.03 g (30 mmol) of triethylamine, 0.112 g (2.50 mmol) of palladium acetate, 0.301 g (5.0 mmol) of tri-*o*-tolylphosphine, 10 mL of acetonitrile, and 0.122 g of *N*-phenyl-2-naphthylamine. The bottle was capped, and the mixture was shaken until it was homogeneous and then heated at 100 °C for 1 h in the steam bath. At this time all of the *p*-bromonitrobenzene had reacted as determined by TLC of the reaction mixture (Alumina, ethyl acetate eluent). The reaction mixture was cooled, the bottle was opened, and 50 mL of water and 50 mL of ether were added. The mixture was stirred and the red solid present was removed by filtration. The solid was recrystallized from hot Me_2SO to give 0.33 g (20%) of bis(*p*-nitrophenyl)-1,3,5-hexatriene, mp 229–231 °C.

The ether layer from the filtrate was separated, dried ($MgSO_4$), and concentrated under reduced pressure. A brown solid was obtained, which was purified by chromatography on alumina (80/20 ether–pentane eluent). The 1-(*p*-nitrophenyl)-1,3,5-hexatriene obtained from the eluate was recrystallized from ethanol to give 1.10 g (54%) of yellow needles of the pure product, mp 110–111 °C.

(*E,E* and *E,Z*)-1-(*p*-Carbomethoxyphenyl)-1,3-pentadiene. A solution of 6.55 g (25 mmol) of methyl *p*-iodobenzoate, 2.04 g (30 mmol) of *trans*-1,3-pentadiene, 0.448 g (2 mmol) of palladium acetate, 1.22 g (4 mmol) of tri-*o*-tolylphosphine, and 12.1 g (120 mmol) of triethylamine was heated in a Pyrex bottle at 100 °C in a steam bath for 15 h. After being cooled, the bottle was opened, 80 mL of water and 80 mL of ether were added, and the mixture was filtered. The residue was washed with 2 × 40 mL of chloroform, the combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure, and the residue was distilled. There was obtained 3.6 g (71%) of the colorless liquid product, bp 140–142 °C (1 mm). The product was found to be an 80:20 mixture of the *E,E* and *E,Z* isomers from its ^1H NMR spectrum (the spectra are given in Table III, supplementary material).

Cyclopalladation of Diiodobis(tri-*o*-tolyl)phosphinepalladium(II). A mixture of 4.68 g (20 mmol) of *p*-iodoanisole, 2.72 g (40 mmol) of isoprene, 0.448 g (2 mmol) of palladium acetate, 1.22 g (4 mmol) of tri-*o*-tolylphosphine, and 6.1 g (60 mmol) of triethylamine in a nitrogen-flushed, capped Pyrex bottle was shaken, warmed until homogeneous, and then heated at 100 °C for 38 h. The reaction mixture was cooled, and 80 mL of water and 100 mL of ether were added. The orange solid formed was separated by filtration and washed with 80 mL of chloroform. There was obtained 0.45 g (42%) of the cyclopalladation product, mp 190 °C dec.

Anal. Calcd for $C_{42}H_{40}I_2P_2Pd_2$: C, 47.00; H, 3.76. Found: C, 46.87; H, 3.57.

From the ether and chloroform solutions, after drying over $MgSO_4$, 1-*p*-anisyl-3-methyl-1,3-butadiene, 1.13 g (32%), bp 120 °C (1.0 mm), mp 76–77.5 °C, could be isolated by vacuum distillation.

1,10-Diphenyl-1,3,5,7-decapentaene. A mixture of 1.83 g (10 mmol) of (*E*)-2-bromostyrene, 0.40 g (5 mmol) of 1,3,5-hexatriene, 0.226 g (1 mmol) of palladium acetate, 0.61 g (2 mmol) of tri-*o*-tolylphosphine, 3.0 g (30 mmol) of triethylamine, and 5 mL of hexamethylphosphortriamide in a nitrogen-flushed capped Pyrex bottle was shaken until homogeneous and heated at 100 °C for 19 h. After being cooled, the reaction mixture was diluted with 5 mL of chloroform, and the insoluble yellow pentaene was removed by filtration. The pentaene product obtained, mp 254–256 °C, weighed 0.18 g (14%).

1-Phenyl-6-piperidino-2,4-hexadiene. A solution of 3.80 g (23 mmol) of bromobenzene, 2.00 g (25 mmol) of 1,3,5-hexatriene, 6.0 g (75 mmol) of piperidine, 0.045 g of palladium acetate, and 0.120 g of tri-*o*-tolylphosphine was prepared in a 200-mL Pyrex pressure bottle. After capping, the bottle was heated in a steam bath 65 h at which time all of the bromobenzene had been consumed as determined by GLC analyses of the reaction mixture. The cooled reaction mixture was treated with 50 mL of 10% sodium hydroxide and the products were extracted with ether. The ether extracts were dried ($MgSO_4$) and concentrated, and the residue was chromatographed on alumina. The first fraction contained 0.1 g (5%) of 1,6-diphenyl-1,3,5-hexatriene. The second fraction, eluted with 90:10 pentane–ether contained a liquid product, which was purified by vacuum distillation, bp 120 °C (0.1 mm). This product proved to be the piperidine adduct. The yield as 1.6 g (30%).

Crystal Data for $C_{22}H_{22}N_2O_4$, the Diels–Alder Adduct of Isoprene with 1,4-Bis(*p*-nitrophenyl)-1,3-butadiene.[17] Crystals of a quality suitable for X-ray diffraction studies were obtained by recrystallization from methanol: monoclinic; a = 19.650 Å, b = 11.666 (3) Å, c = 20.460 (3) Å, β = 123.79 (2°, V = 3898.1 (16)°, Z = 8, d(calcd) = 1.289, space group, $C2/c$. The data crystal, which measured 0.05 × 0.12 × 0.6 mm, was cleaved from a long colorless neele. The small cross-sectional area of this crystal resulted in very low diffraction intensities; data collection was attempted only to $2\theta = 40°$ (Mo K_α). A total of 1989 reflections were collected (one form, $\pm h,k,l$), yielding 1804 unique reflectons (averaging of redundant data produced agreement at the 2% level) and 1135 reflections with $I \geq 2\sigma(I)$. This set of reflections was used in the subsequent structure solution and refinement.

The structure was solved without difficulty by using the direct-methods program SOLV; all but four of the 28 non-hydrogen atoms were found on the resulting E map, the remainder being obtained from a subsequent difference Fourier synthesis. Insufficient data existed to allow refinement of all non-hydrogen atoms with anisotropic thermal parameters; anisotropic refinement was restricted to the N, O, and aliphatic C atoms. Hydrogen atoms were included in idealized positions (d(C–H) = 0.96 Å, $U = 1.2 \times U$ for bonded carbon). Refinement converged at R_F = 7.92%, R_{wF} = 7.94%, and GOF = 1.29, with the highest peak on the final difference map = 0.32 e $Å^{-3}$. The final data/parameter ratio was 6.0. Complete data are given in Tables IV–IX in the supplementary material.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant No. CHE-8006319. Palladium acetate was kindly loaned to us for this study by the Johnson Matthey Company.

Supplementary Material Available: Table III containing the melting points, NMR spectra, UV spectra, and molecular weights for the compounds prepared in this study and Tables IV–IX containing crystallographic data for the Diels–Alder adduct of isoprene with 1,4-bis(*p*-nitrophenyl)-1,3-butadiene (19 pages). Ordering information is given on any current masthead page.

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(17) The crystallographic data were collected and interpreted by Dr. Arnold Rheingold of this department.