Registry No.—**1b**, 67938-50-5; **2b**, 67938-51-6; **2c**, 40630-06-6; **3**, 67938-52-7; **4**, 5437-45-6; dibutylamine, 111-92-2; benzyl chloride, 100-44-7; tryptamine, 61-54-1.

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(5) E.g., F. Drahowzakl and D. Klamann, *Monatsh. Chem.*, **82**, 588 (1951).

Palladium-Catalyzed Arylation of Conjugated Dienes

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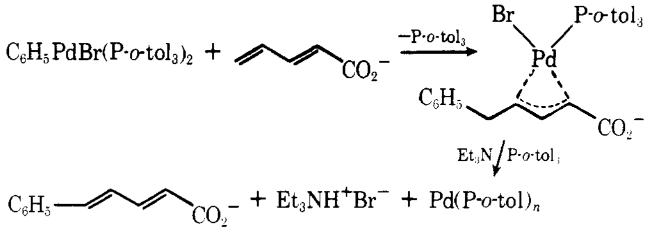
The palladium-catalyzed arylation of simple olefins with aryl halides is a versatile and convenient method for the synthesis of arylated olefins.[1] Similar reactions with conjugated dienes would be expected to produce arylated dienes. Some differences and perhaps complications could be expected, however, since π-allylic palladium species probably would be intermediates in the reaction.[2] We now report a study of this reaction.

Results and Discussion

It was anticipated from previous results[3] that aryl halides and dienes conjugated with carbonyl groups would react under our usual conditions catalytically to produce arylated dienes. This proved to be the case with (*E*)-2,4-pentadienoic acid. Bromobenzene and the pentadienoic acid reacted with 1 mol % of palladium acetate, 2 mol % of tri-*o*-tolylphosphine, and 2 equiv of triethylamine at 100 °C in 20 h to form (*E,E*)-5-phenyl-2,4-pentadienoic acid in 92% (isolated) yield. We believe that a π-allylic palladium(II) intermediate is involved which readily undergoes elimination of the palladium hydride group because of the activating influence of the neighboring carboxylic acid (anion) group. 3,4-Methylenedioxybromobenzene reacts analogously, forming (*E,E*)-piperic acid in 60% yield. Sorbic acid and bromobenzene reacted poorly under a variety of conditions, giving mixtures of products which were not characterized.

$$C_6H_5Br + Pd(P\text{-}o\text{-}tol_3)_n \longrightarrow C_6H_5Pd(Br)(P\text{-}o\text{-}tol_3)_2 + (n-2)P\text{-}o\text{-}tol_3$$



trans-β-Bromostyrene and (*E*)-2,4-pentadienoic acid reacted normally to form (*E,E,E*)-7-phenyl-2,4,6-heptatrienoic acid in 57% yield in 4 h. These and other reactions are summarized in Table I.

Conjugated dienes without the activating carbonyl group reacted less well under the above conditions. The catalyst apparently was converted into relatively stable π-allylic complexes which either decomposed slowly or not at all under the reaction conditions. This problem was partially overcome by using larger amounts of catalyst. For example, iodobenzene and isoprene gave a 52% yield of 1-phenyl-3-methyl-1,3-butadiene (phenylisoprene) when 5% palladium acetate and 10% triphenylphosphine were employed as the catalyst and triethylamine as the base. As in the reactions of vinylic halides with mono olefins reported previously[4] the aryl halide–con-

Table I. Arylation Reactions of Conjugated Dienes[a]

aryl halide, mmol	registry no.	diene, mmol	registry no.	amine, mmol	phosphine	time, h	products, % yield[b]	registry no.
bromobenzene, 10	108-86-1	(*E,E*)-2,4-pentadienoic acid, 10	21651-12-7	$(C_2H_5)_3N$, 25	P(*o*-tol)$_3$	20	(*E,E*)-5-phenyl-2,4-pentadienoic acid, 92	28010-12-0
3,4-methylenedioxybromobenzene, 10	2635-13-4	(*E,E*)-2,4-pentadienoic acid, 10		$(C_2H_5)_3N$, 25	P(*o*-tol)$_3$[c]	24	(*E,E*)-5-(3′,4′-methylenedioxyphenyl)-2,4-pentadienoic acid, 60	136-72-1
(*E*)-β-bromostyrene, 10	588-72-7	(*E,E*)-2,4-pentadienoic acid, 10		$(C_2H_5)_3N$, 25	P(*o*-tol)$_3$	4	(*E,E,E*)-7-phenyl-2,4,6-heptatrienoic acid, 57	10576-63-3
iodobenzene, 10	591-50-4	isoprene, 30	78-79-5	$(C_2H_5)_3N$, 35	PPh$_3$[d]	18	(*E*)-1-phenyl-3-methyl-1,3-butadiene, 52	68036-69-1
bromobenzene, 10		isoprene, 12.5		piperidine,[h] 300	P(*o*-tol)$_3$	48	(*E*)-1-phenyl-3-methyl-1,3-butadiene, 35	
							N-1-(4-phenyl-2-methyl-2-butenyl)piperidine, 57	68036-70-14
bromobenzene, 10		1,3-cyclohexadiene, 15	592-57-4	piperidine, 300	PPh$_3$	16	phenylcyclohexadienes, 13[e]	
							3-phenyl-6-piperidino-1-cyclohexene, 51	68036-71-5
							4-phenyl-3-piperidino-1-cyclohexene, 2	68036-72-6
							1,4-diphenyl-1,3-cyclohexadiene, 2	10345-94-5
4-bromoanisole, 10	104-92-7	(*E*)-1,3-pentadiene, 25	2004-70-8	morpholine,[h] 300	PPh$_3$	8	1-*p*-anisyl-1,3-pentadiene, 57	3909-98-6
							1-*p*-anisyl-4-morpholino-3-pentene, 12[f]	68036-73-7
3-bromopyridine, 50	626-55-1	1,3-butadiene, 125	106-99-0	morpholine, 150	P(*o*-tol)$_3$	3	1-(3′-pyridyl)-4-morpholino-2-butene, 60[g]	68036-74-8

[a] 1 mol % of palladium acetate and 2 mol % of triarylphosphine based upon the aryl halide were used as catalyst except where noted. [b] Yields of isolated products. [c] 6 mol % of tri-*o*-tolylphosphine was used in this reaction with 1 mol % of $Pd(OAc)_2$. [d] 5 mol % of palladium acetate and 10 mol % of triphenylphosphine were used as catalyst in this example. The experiment was carried out by H. A. Dieck. [e] Two isomers present. The UV spectra of samples isolated by preparative GC indicate that they are 1-phenyl-1,3-cyclohexadiene and 3-phenyl-1,4-cyclohexadiene (registry no. 15619-32-6 and 4794-05-2, respectively). [f] 22% of 4-bromoanisole was recovered in this reaction. Yields of products are based on the total amount of 4-bromoanisole initially added. [g] 4 mmol of *N*-1-(2,7-octadienyl)morpholine (registry no. 25017-06-5) was also isolated. [h] Registry no.: piperidine, 110-89-4; morpholine, 110-91-8.

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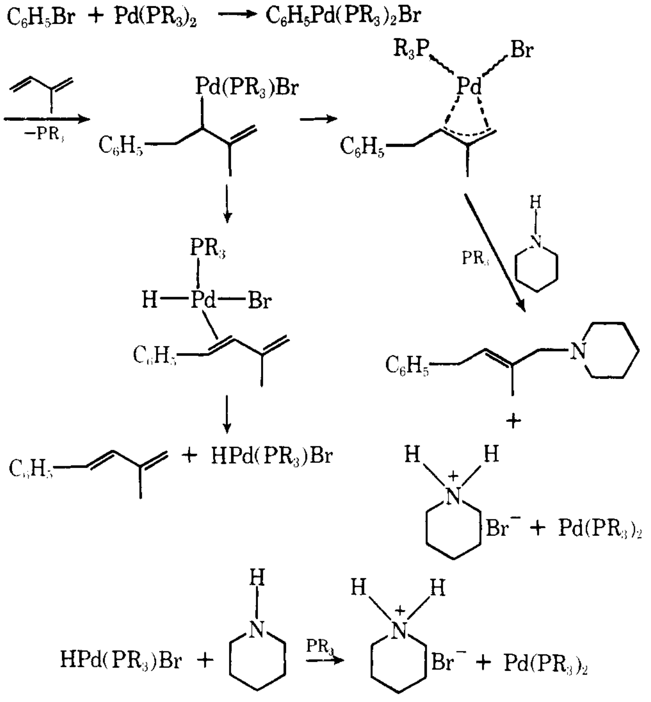
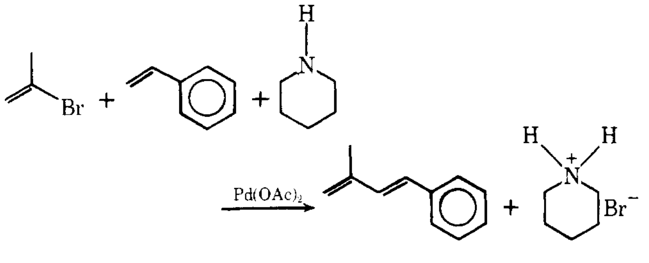
Scheme I



jugated diene reactions proceeded more rapidly with a basic secondary amine than with triethylamine, but as in the mono olefin reactions also, the products contained amine adducts. The explanation is that intermediate π-allylic complexes undergo decomposition by reaction with the secondary amine. The use of the hindered nonnucleophilic base diisopropylamine gives essentially the same result as with triethylamine in this reaction. In the aryl halide–conjugated diene reactions π-allylic complexes can be formed directly, while in the vinylic halide–mono olefin reaction a palladium hydride addition and readdition had to occur first. We believe that the bromobenzene–isoprene–piperidine reaction occurs according to Scheme I. In this reaction, phenylisoprene was obtained in 35% yield and the amine adduct in 57% yield. The amine adduct could be easily converted into phenylisoprene in high yield simply by adding methyl iodide to form the quaternary salt and then warming it with aqueous base.

We also prepared phenylisoprene by an alternative palladium-catalyzed route to compare with the above method. The reaction of 2-bromopropene and styrene with piperidine as base gave a 67% yield of phenylisoprene and less than 2% of the amine adduct of the diene in 11 h at 100 °C. Since the conjugated diene would necessarily need to be an intermediate for the formation of the amine adduct, less amine is formed than in the above reaction where the π-allylic complex is formed directly.



1,3-Cyclohexadiene reacted analogously with bromobenzene and piperidine. The major product, 41%, was 3-phenyl-6-piperidino-1-cyclohexene. About 2% of the allylic isomer, 4-phenyl-3-piperidino-1-cyclohexene, was also found. A mixture of about equal amounts, 13% total, of two phenylcyclohexadienes was isolated as well as 2% of 1,4-diphenyl-1,3-cyclohexadiene. The UV spectra of the phenylcyclohexadienes isolated by preparative GLC indicate that the products were the 1-phenyl-1,3-cyclohexadiene and 3-phenyl-1,4-cyclohexadiene. Since these isomers were not obtained completely pure, we are not certain of their identity. If the latter product is correctly identified, it seems probable that the phenylpalladium group is adding to a small extent in the reverse direction to that required for formation of the other reaction products.

Examples of the reaction with 4-bromoanisole and 3-bromopyridine are also included in the table.

We have used either triphenylphosphine or tri-*o*-tolylphosphine in these reactions. There is generally little difference between them except when aryl bromides with strongly electron-releasing groups are present.[1]

The variety of successful reactions carried out suggests that this is a very general synthetic method. Since the amine adducts can be converted into conjugated dienes by the Hoffmann elimination or to allylic halides by the von Braun reaction, the diene arylation provides a very convenient method for adding four or more carbons to aromatic rings.

Experimental Section

Reagents. The organic halides employed were all commercial products used as received except for 3,4-methylenedioxybromobenzene. The last compound was prepared by brominating 1,2-methylenedioxybenzene.[5] Except for 2,4-pentadienoic acid, the dienes used were commercial samples also. The 2,4-pentadienoic acid was prepared by the reaction of acrolein with malonic acid.[6] The amines were dried with 4 Å molecular sieves before use. Triphenylphosphine was used as received from the Aldrich Chemical Co., and tri-*o*-tolylphosphine was prepared as described previously.[1] Palladium acetate was prepared from palladium black as described by Wilkinson et al.[7]

General Procedure for the Arylation of Conjugated Dienes. The palladium acetate and triarylphosphine were weighed into a thick-walled "Pyrex" bottle, the amine, organic halide, and diene were added, and the bottle was capped under nitrogen. In the butadiene reaction, a 60 mL stainless steel bomb was used and the reactants were cooled in dry ice to prevent evaporation before sealing. The reaction mixtures were then warmed with shaking until they were homogeneous and heated at 100 °C until GLC analysis of a small sample showed that the organic halide had all reacted. The reactions with the pentadienoic acid were diluted with cold dilute hydrochloric acid and extracted with several portions of methylene chloride. After drying, the extracts were concentrated under reduced pressure at 25 °C and the residues were recrystallized. The other reactions were diluted with ether and aqueous base. The ether extracts were washed several times with water to remove the excess reactant amines, dried, and distilled under reduced pressure through a short Vigreux column. Purity of the products prepared and spectra are given in Table II (see supplementary material).

Phenylisoprene from 2-Bromopropene and Styrene. A mixture of 0.022 g (0.1 mmol) of palladium acetate, 0.061 g (0.2 mmol) of tri-*o*-tolylphosphine, 1.21 g (10 mmol) of 2-bromopropene, 1.25 g (12.0 mmol) of styrene, and 2.55 g (30 mmol) of piperidine was shaken until it was homogeneous in a capped "Pyrex" tube under nitrogen and then heated at 100 °C for 11 h. After cooling, 1-methylnaphthalene was added as an internal standard and the products were analyzed by GLC. There was found a 67% yield of phenylisoprene and less than 2% of the piperidine adduct of the phenylisoprene. The yield of phenylisoprene slowly decreases on longer heating of the reaction mixture.

Acknowledgment. We thank the National Science Foundation for support of this research and the Matthey-Bishop Co., Inc., for the loan of the palladium used in the catalysts.

Registry No.—phenylisoprene, 2288-18-8; 2-bromopropene, 557-93-7; styrene, 100-42-5.

Supplementary Material Available: Table II, containing boiling points, molecular weights, and NMR spectra of the products prepared (2 pages). See any current masthead page for ordering information.

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(2) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5542 (1968).
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Selective Cleavage of 1-Methoxy-2-(phenylthio)cyclopropane Homologues by Electrolytic Procedure

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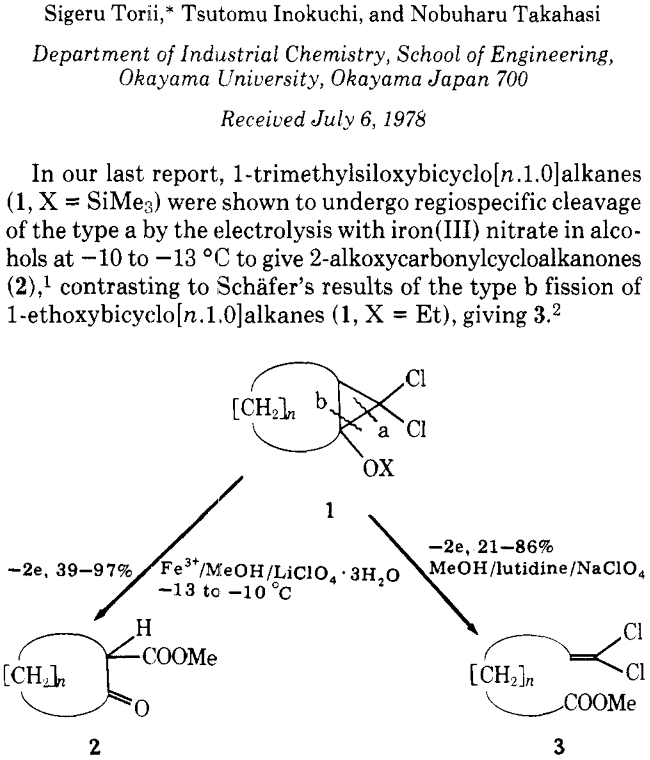
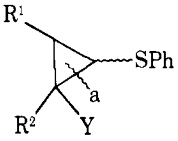
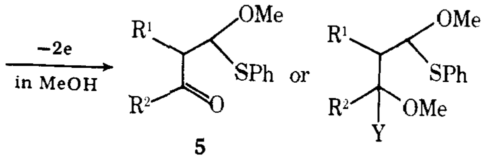
In our last report, 1-trimethylsiloxybicyclo[*n*.1.0]alkanes (**1**, X = $SiMe_3$) were shown to undergo regiospecific cleavage of the type a by the electrolysis with iron(III) nitrate in alcohols at −10 to −13 °C to give 2-alkoxycarbonylcycloalkanones (**2**),[1] contrasting to Schäfer's results of the type b fission of 1-ethoxybicyclo[*n*.1.0]alkanes (**1**, X = Et), giving **3**.[2]



We report in this paper that the type a ring opening of 1-methoxy-2-(phenylthio)cyclopropanes (**4**)[3] can be carried out anodically under a constant applied voltage in a two-compartment cell in the presence of potassium carbonate. The reaction provides a convenient procedure for the preparation of 2-[methoxy(phenylthio)methyl]alkanone analogues **5** or **6**.[4]



4



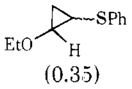
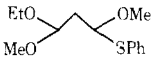
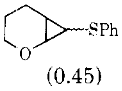
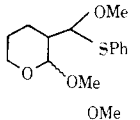
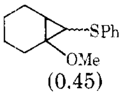
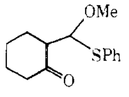
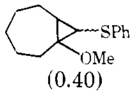
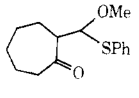
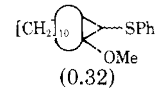
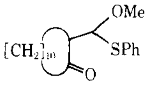
5

6a, Y = OEt
b, Y = OMe

Electrolysis of a solution of **4** ($R^1 = R^2 = -(CH_2)_4-$, 0.43 mmol) and tetraethylammonium tosylate in methanol in the presence of potassium carbonate (50–120 mg) in an anode compartment (cell voltage 3 V, anode potential 0.9 V vs. SCE,[5] 0.8–1.2 mA/cm^2) consumed 5.8 F/mol, affording **5** in 98% yield (75% of conversion). The electrolysis conditions of **4**, conversion percentages, and yields of **5** and **6** are listed in Table I.

When **4** ($R^1 = R^2 = H$; Y = OEt) was electrolyzed without potassium carbonate it was converted into **6b** ($R^1 = R^2 = H$; Y = OMe) in 72% yield as well as ~20% of diphenyl disulfide after passage of 2.3 F/mol. Since on continuing the electrolysis the solution becomes weakly acidic, the acetal **6a** initially formed would undergo trans acetalization to form **6b**. However, analogous electrolysis with appreciable amounts of potassium carbonate provided **6a** ($R^1 = R^2 = H$; Y = OEt) in 93% yield as a sole product. The latter results suggest that the intermediate **7a**, generated by one-electron discharge on the anode, could be trapped immediately with methanol without scrambling of alkoxides. In the conditions of the formation of **6b**, partially generated thiophenol would also be oxidized

Table I. Conditions and Results of Electrolysis of 1-Methoxy-2-(phenylthio)cyclopropane Homologues in Methanol[a]

entry	substrate 4 (mmol)	registry no.	current, mA/cm^2	applied voltage, V	F/mol	conversion, %	product 5 or 6	registry no.	yield,[b] %
1	 (0.35)	52565-43-2	0.8–1.2	3	4.0	100		68002-01-7	93
2	 (0.45)	68036-09-9	0.8–1.2	3	3.5	89		68002-02-8	82
3	 (0.45)	68001-98-9	0.8–1.2	3	5.8	75		68002-03-9	98
4	 (0.40)	68001-99-0	0.8–1.2	4	2.3	100		68002-04-0	79
5	 (0.32)	68002-00-6	0.8–1.2	5	2.3	100		68002-05-1	78

[a] Electrolyzed using a divided cell fitted with platinum electrodes in the presence of Et_4NOTs at 20–30 °C for 6–12 h. [b] Based on isolated product.

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