J. Org. Chem. **1983**, *48*, 1333–1336

product were identical with both the material produced in the other sequence and with the sample supplied by Dr. Kende. A mixed melting point was undepressed.

Acknowledgment. We express our appreciation to Dr. Andrew Kende for generously providing us with a sample of quinone **16**. This work was generously supported by the National Cancer Institute of the National Institutes of Health (Grant No. CA 18141).

Registry No. *cis*-**5**, 80727-33-9; *trans*-**5**, 84810-55-9; *cis*-**7a**, 84810-56-0; *trans*-**7a**, 84810-57-1; *cis*-**7b**, 84810-58-2; *trans*-**7b**, 84810-59-3; **8**, 81838-64-4; **9**, 78-94-4; *cis*-**10a**, 84810-60-6; *trans*-**10a**, 84810-61-7; **10b**, 84810-62-8; **10c**, 84810-63-9; *cis*-**11**, 84810-64-0; *trans*-**11**, 84810-65-1; **12a**, 84810-66-2; **12b**, 84810-67-3; *cis*-**13**, 84810-68-4; **14**, 84810-69-5; **15**, 84810-70-8; **16**, 77219-86-4; **17**, 84810-71-9; **18**, 84810-72-0; **19**, 84810-73-1.

Reaction of Diazonium Salts with Transition Metals. 8. Palladium-Catalyzed Carbon–Carbon Coupling of Arenediazonium Salts with Organotin Compounds[1]

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Received May 3, 1982

Arenediazonium salts are effectively functionalized with a methyl or vinyl group by palladium-catalyzed coupling with organotin compounds in acetonitrile at room temperature. Fairly good yields were obtained irrespective of the nature of a substituent on the aromatic ring, including a nitro group. Transformation of the diazonium group can proceed chemoselectively even in the presence of halogen substituents.

Although the diazonium group is useful to introduce various functional groups into an aromatic ring, simple alkyl groups have rarely been introduced. Unlike heteroatom nucleophiles, carbon nucleophiles such as active methylene compounds,[2] Grignard reagents,[3] and active aromatic rings react with diazonium salts to give azo compounds. The conventional C–C bond-forming reactions via diazonium salts have been achieved under copper catalysis (Meerwein arylation and Sandmeyer cyanation) or under basic conditions (Gomberg reaction), in which the mechanism is believed to take a radical pathway.[4] Recent palladium-catalyzed reactions of diazonium salts with alkenes[5] or carbon monoxide,[6] in which arylpalladium species are assumed to be intermediates, afforded a simple method for transformation of the C–N bond to a C–C bond. The palladium-catalyzed reactions have several advantages over the conventional methods such as higher yields and less restriction of substituents on both substrates.

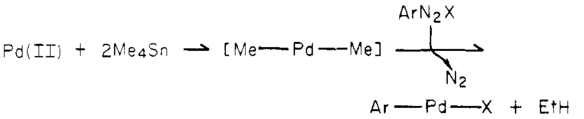
We now report a simple C–C coupling of arenediazonium salts (ArN_2X) utilizing metathesis between in situ formed arylpalladium species and tetraorganotin compounds.

Results and Discussion

Methylation of ArN_2X. Addition of a palladium catalyst to a solution of an ArN_2X and Me_4Sn in acetonitrile afforded a methylarene (ArMe) with gas evolution (eq 1).

$$ArN_2X + Me_4Sn + PdL_2 \rightarrow ArMe\ (+\ Ar\text{–}Ar + EtH) \quad (1)$$

The effects of reaction conditions to the methylation of $4\text{-}BrC_6H_4N_2X$ are shown in Table I. Presence of chloride ion (by the use of ArN_2Cl or an addition of LiCl) in the reaction produced Me_3SnCl and decreased the yield drastically (entry 1 and 3). In the presence of Me_3SnCl, ArN_2X formed intractable tarry materials. Both zero- and divalent palladium complexes acted as catalysts effectively, albeit palladium(II) acetate showed an induction period of about 15 min as shown in Figure 1. Since palladium(II) acetate does not react with ArN_2X, the induction period (and also the deviation between the course of ArMe formation and gas evolution) may be explained in terms of formation of dimethylpalladium followed by reaction with ArN_2X to give ethane and ArPdX as a preceding step of the reaction (eq 2). A GLC analysis of the gas evolved



$$\mathrm{Pd(II)} + 2Me_4Sn \rightarrow [Me\text{—}Pd\text{—}Me] \xrightarrow[\searrow N_2]{ArN_2X} Ar\text{—}Pd\text{—}X + EtH \quad (2)$$

under the normal reaction conditions revealed that it contained about 8 vol % of hydrocarbon composed of ethane (~95%) and methane (~5%).

In the absence of ArN_2X, the reaction of Me_4Sn and $Pd(OAc)_2$ at 25 °C also gave gaseous products along with precipitation of palladium black. However, the composition of hydrocarbons in the gas was very different, i.e.: methane, 57%; ethane, 36%; ethylene, 7%.[7] Thus, the dimethylpalladium may react directly with ArN_2X to form ethane and ArPdX.[8]

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[7] The yield of ethylene depended on $Pd(OAc)_2$ concentration (7.5% based on Pd at $[Pd(OAc)_2]$ = 0.032 M and 13% at 0.098 M), while those of methane and ethane did not (methane 59% and ethane 37.5% at 0.032 M and methane 57% and ethane 37% at 0.098 M). Although there is no other evidence, the formation of ethylene and its dependence on $Pd(OAc)_2$ concentration suggest the presence of α-elimination process for decomposition of dimethylpalladium complex in the absence of ArN_2X.[20]

[8] These results suggest electron transfer from dimethylpalladium for the present reductive coupling reaction,[21] i.e.: $Pd^{II}Me_2 + ArN_2X \rightarrow [Pd^{III}Me_2]^+ + ArN_2\cdot + X^- \rightarrow EtH + Pd(I) + Ar\cdot + X^- + N_2 \rightarrow EtH + ArPdX + N_2$

0022-3263/83/1948-1333\$01.50/0

Table I. Effects of Reaction Conditions on the Methylation of 4-$BrC_6H_4N_2X$[a]

no.	X in 4-$BrC_6H_4N_2X$	catalyst (mol %)	solvent	temp, °C	yields, %[b]
1	Cl	$Pd(OAc)_2$ (10)	CH_3CN	25.4	4
2	BF_4	$Pd(OAc)_2$ (10)	CH_3CN	25.4	83
3	BF_4 + LiCl	$Pd(OAc)_2$ (10)	CH_3CN	25.4	20
4	PF_6	$Pd(OAc)_2$ (10)	CH_3CN	25.4	78
5	PF_6	$Pd(OAc)_2$ (2)	CH_3CN	25.4	79
6	PF_6	$Pd(OCOCF_3)_2$ (10)	CH_3CN	25.4	76
7	PF_6	$Pd(dba)_2$[c] (10)	CH_3CN	25.4	74
8	PF_6	$Pd(OAc)_2$ (10)	CH_3CN	0	0
9	PF_6	$Pd(OAc)_2$ (10)	CH_3CN	40	84
10	PF_6	$Pd(OAc)_2$ (10)	CH_2Cl_2	25.4	32

[a] Reactions were carried out by an addition of a catalyst to a solution of ArN_2X (0.5 mmol) and Me_4Sn (0.6 mmol) in 2 mL of acetonitrile in a thermostatted cell. [b] GLC yields of 4-bromotoluene are based on ArN_2X. [c] Bis(dibenzylideneacetone)palladium(0).

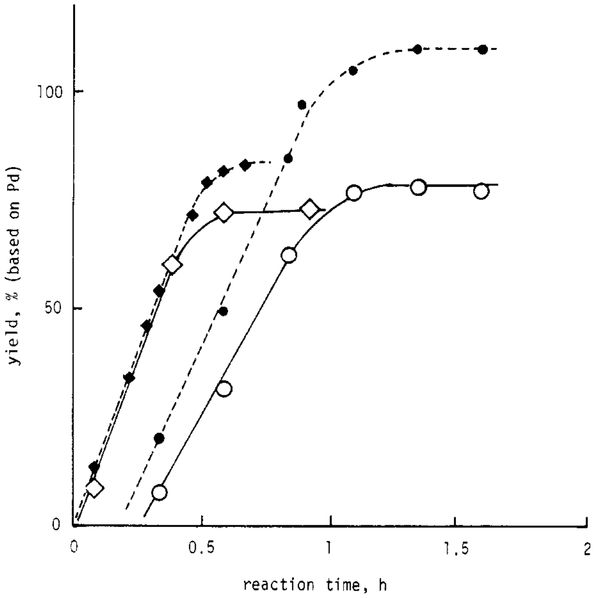
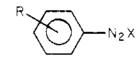
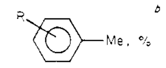


Figure 1. Time course of methylation of 4-$BrC_6H_4N_2PF_6$ by Me_4Sn in CH_3CN at 25.4 °C with 10 mol % of a palladium catalyst: ○ and ◇, formation of 4-bromotoluene; ● and ◆, gas evolution; ○ and ●, with $Pd^{II}(OAc)_2$; ◇ and ◆, with $Pd^0(dba)_2$ [bis(dibenzylideneacetone)palladium].

Table II. Methylation of ArN_2X by Me_4Sn[a]

no.	R in 	X	yields of [b]
11[c]	H	BF_4	55
12	2-Me	BF_4	0[d]
13	3-Me	BF_4	34[e]
14	4-Me	BF_4	59
15	2-Cl	BF_4	64
16	3-Cl	BF_4	89
17	4-Cl	BF_4	88
18	4-Br	PF_6	76
19	4-Br	BF_4	(38)
20	2-NO_2	PF_6	94
21	3-NO_2	PF_6	(62)
22	4-NO_2	PF_6	95
23	4-NO_2	BF_4	(54)

[a] Reactions were carried out by an addition of 0.05 mmol of $Pd(OAc)_2$ to a solution of Me_4Sn (0.6 mmol), ArN_2X (0.5 mmol), and 2 mL of CH_3CN at room temperature for 2 h. [b] GLC yields are based on ArN_2X. A few percent of Ar-Ar was also formed. The yields in parentheses are isolated and purified yields with the use of 10 mmol of ArN_2X, 12 mmol of Me_4Sn, 1 mmol of $Pd(OAc)_2$, and 50 mL of CH_3CN. [c] $Pd^0(dba)_2$ (0.05 mmol) was used instead of $Pd(OAc)_2$. [d] Aceto-*o*-toluide was formed. [e] About 20% of 3,3′-dimethyl biphenyl and aceto-*m*-toluide were also formed.

At 0 °C the reaction did not proceed. In dichloromethane, the reaction and gas evolution started smoothly, but the formation of 4-bromotoluene stopped in a short time.

Table II shows the typical results obtained from the reaction of various ArN_2X with Me_4Sn by using $Pd(OAc)_2$ as a catalyst in acetonitrile for 2 h at room temperature. Most of the reactions were completed within 1 h. Substituents on aromatic ring except for the *o*-methyl group did not affect the reaction materially. *o*-Methylbenzenediazonium salt gave aceto-*o*-toluide as an isolable product. The amide is considered to form by the reaction of the diazonium salt with acetonitrile (eq 3). Methyl group at

$$ArN_2^+ + CH_3CN \rightarrow [CH_3\text{-}C{\equiv}N^+\text{-}Ar] \xrightarrow{H_2O} CH_3CONHAr \quad (3)$$

the ortho position has been known to direct favorably toward the formation of the *N*-aryl nitrilium ion.[9]

The palladium-catalyzed reaction of PhN_2BF_4 with Et_4Sn proceeded very slowly and gave only a 7% yield of ethylbenzene along with 1% of styrene after 1 day at room temperature in acetonitrile. A GLC analysis of the evolved gas showed the formation of ethylene, ethane, and butane in the percent ratio of 98%, 2%, and a trace, respectively, in the presence of $Pd(OAc)_2$ catalyst. The formation of ethylene is reasonably explained by β-hydride elimination of an ethylpalladium intermediate (eq 4), and the resulting

$$\text{Ar-Pd-X} + Et_4Sn \rightarrow [\text{Ar-Pd-Et}] \xrightarrow{\beta\text{-hydride elimination}} \text{Ar-Pd-H} + CH_2{=}CH_2 \xrightarrow{\text{reductive elimination}} \text{Ar-Et} + \text{Pd(0)} \quad (4)$$

ethylene would be the source of styrene in the palladium-catalyzed phenylation by PhN_2BF_4. Tetrabutyltin did not react under the present reaction conditions.

Vinylation of ArN_2X. When a palladium catalyst was added to a solution of PhN_2BF_4 and $CH_2{=}CHSnBu_3$ in acetonitrile, gas evolution was immediate and complete within 1 min. Quantitative analysis of the solution by GLC showed the formation of styrene, biphenyl, and a trace of stilbene. Disproportionation of phenylpalladium may produce biphenyl (eq 5). Stilbene can be formed by the

$$2\text{Ph-Pd-X} \rightleftharpoons PdX_2 + \text{Ph-Pd-Ph} \rightarrow \text{Ph-Ph} \quad (5)$$

reaction of phenylpalladium and styrene, a primary

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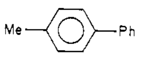
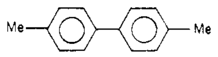
Table III. Vinylation of PhN_2BF_4 by CH_2=$CHSnBu_3$ [a]

no.	CH_2=$CHSnBu_3$/ PhN_2BF_4 ratio[b]	catalyst (mol %)[c]	% product[d]	
			PhCH=CH_2	PhPh
24	1	$Pd(OAc)_2$ (10)	44	36
25	0.5	$Pd(OAc)_2$ (10)	21	22
26	2	$Pd(OAc)_2$ (10)	44	13
27	1	$Pd(OAc)_2$ (2)	49	21
28	1	$Pd(OAc)_2$ (1)	49	18
29	1	$Pd(dba)_2$ [e] (10)	41	50
30	1	$Pd(dba)_2$ [e] (1)	53	18
31	2	$Pd(dba)_2$ [e] (1)	80	0
32	1	none	2.5[f]	0

[a] Reactions were carried out by an addition of a catalyst to a solution of PhN_2BF_4 and CH_2=$CHSnBu_3$ in acetonitrile at room temperature for 5 min. [b] Molar ratios. [c] Based on PhN_2BF_4. [d] GLC yields based on PhN_2BF_4. [e] Bis(dibenzylideneacetone)palladium(0). [f] After 1 h.

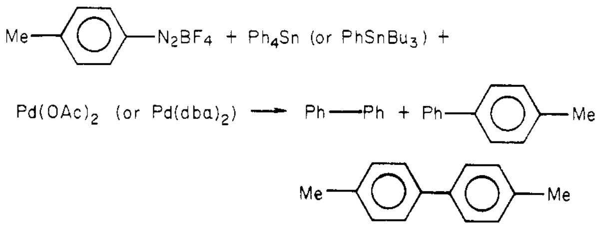
Table IV. Phenylation of $4\text{-}MeC_6H_4N_2BF_4$ [a]

no.	Ph-Sn	catalyst	atmosphere	% products[b]		
				Ph-Ph		
33	Ph_4Sn	$Pd(OAc)_2$	aerobic	57	16	1
34	$PhSnBu_3$	$Pd(OAc)_2$	aerobic	12	48	7
35	$PhSnBu_3$	$Pd(OAc)_2$	nitrogen	11	59	7
36	$PhSnBu_3$	$Pd(OAc)_2(PPh_3)_2$	nitrogen	21	23	7
37	$PhSnBu_3$	$Pd(dba)_2$ [c]	nitrogen	8	66	3

[a] Reactions were carried out by an addition of a catalyst (10 mol %) to a solution of $4\text{-}MeC_6H_4BF_4$ and a tin compound in CH_3CN at room temperature. [b] GLC yields based on $4\text{-}MeC_6H_4N_2BF_4$. [c] Bis(dibenzylideneacetone)palladium(0).

product. Table III shows the effects of reaction conditions on the vinylation. Interestingly, the smaller amount of the catalyst gave a better yield of styrene. In the presence of excess CH_2=$CHSnBu_3$ and 1 mol % of $Pd^0(dba)_2$, an 80% yield of styrene was obtained with a substantial decrease of biphenyl. Thus, the present reaction can be expected as a convenient method to prepare styrene derivatives.

Phenylation of ArN_2X. The coupling reaction of $4\text{-}MeC_6H_4N_2BF_4$ with a phenyltin compound gave biphenyl derivatives (eq 6). With zerovalent palladium and



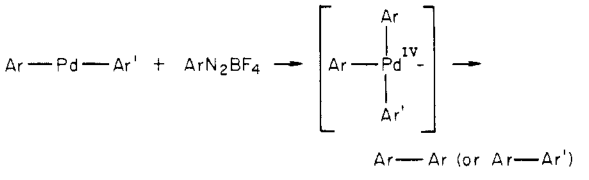
(6)

$Pd(dba)_2$ = bis(dibenzylideneacetone)palladium(0)

$PhSnBu_3$ under a nitrogen atmosphere, the cross-coupling product was favorably obtained. However, the contamination with other isomers could not be depressed effectively in all reactions examined as shown in Table IV. The inevitable formation of homo coupling products might be accounted for by the rapid exchange reaction between arylpalladium species (eq 7) or a tetravalent palladium

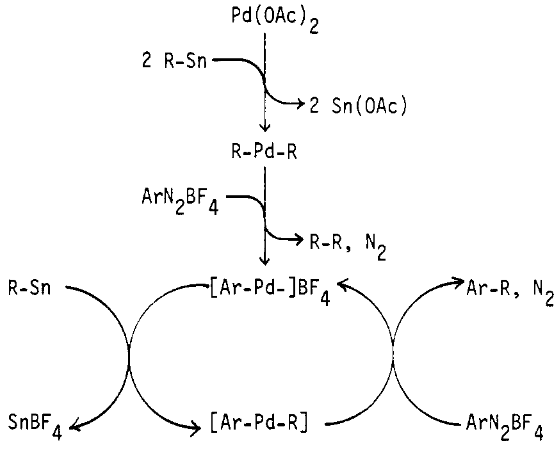
$$\mathrm{Ar{-}Pd{-}Ar'} + \mathrm{Ar{-}Pd{-}} \rightarrow \mathrm{Ar{-}Pd{-}Ar} + \mathrm{Ar'{-}Pd{-}} \quad (7)$$

intermediate, which was proposed in the palladium-catalyzed coupling or organohalides and organotin compounds,[10] as in eq 8.



$$\mathrm{Ar{-}Pd{-}Ar'} + \mathrm{ArN_2BF_4} \rightarrow \left[\mathrm{Ar{-}}\overset{\mathrm{Ar}}{\underset{\mathrm{Ar'}}{\mathrm{Pd}^{IV}}}\mathrm{{-}}\right] \rightarrow \mathrm{Ar{-}Ar\ (or\ Ar{-}Ar')} \quad (8)$$

Scheme I



Although the detailed and exact reaction mechanism of the present reaction is still unknown, the principal reaction pathway can be depicted as in Scheme I.

To our knowledge this is the first example of direct substitution of a diazonium group by a methyl group. The excellent yields of nitrotoluenes are notable because a nitro group on an aromatic ring interferes in a conventional alkylation such as Friedel–Crafts alkylation or the Grignard coupling reaction.[11] The inertness of a nitro group in the present method may provide utility in synthetic organic chemistry in view of the versatility of nitro group in functional group transformation via an amino group. Haloarenes are frequently used in palladium-catalyzed reactions of aromatics.[12-14] In the present reaction, how-

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ever, halogen substituents do not enter into the reaction because of the high reactivity of the diazonium group. Thus, ArN_2X can be utilized as excellent precursors for the chemoselective preparation of arylpalladium species bearing a halogen group.

Experimental Section

Materials. Acetonitrile was distilled from phosphorus pentoxide (twice) and calcium hydride under nitrogen. Liquid arylamines were distilled before use under nitrogen. Guaranteed reagents of crystalline arylamines were used as received. Arenediazonium tetrafluoroborates,[15] hexafluorophosphates,[16] and chloride[17] were prepared by the ordinary methods and stored under nitrogen at −20 °C. Palladium acetate,[18] palladium trifluoroacetate,[18] bis(triphenylphosphine)palladium acetate,[18] and bis(dibenzylideneacetone)palladium[19] were prepared by the published method. Tetramethyltin and Et_4Sn were prepared by the reactions of $SnCl_4$ with MeMgBr in dibutyl ether and EtMgBr in diethyl ether, respectively. Phenyltributyltin and $CH_2{=}CHSnBu_3$ were prepared by the reactions of Bu_3SnCl with PhMgBr and $CH_2{=}CHMgBr$, respectively. Tetraphenyltin and Bu_3SnCl were used as received.

General Procedure. To a solution of an ArN_2X (0.5 mmol), a tin compound (0.6 mmol), and 2 mL of CH_3CN was added 0.05 mmol of a palladium catalyst at room temperature. After 2 h (for Me_4Sn, or 5 min for $CH_2{=}CHSnBu_3$) of stirring, an appropriate internal standard (from decane to octadecane) and 2 mL of chloroform were added to the solution. The reaction mixture was directly analyzed by GLC (silicone SE-30). The structures of all products were confirmed by comparison of the retention times on GLC with those of authentic samples (commercial origin). Some toluene derivatives were isolated by using 10 mmol of an ArN_2X, 12 mmol of Me_4Sn, 1 mmol of $Pd(OAc)_2$, and 50 mL of CH_3CN (entries 19, 21, and 23). The structure of the isolated products was confirmed by the comparison of their IR and NMR spectra with those of authentic samples.

Time Course of the Methylation. The reactions were started by addition of 2 mL of CH_3CN to a mixture of 0.5 mmol of $4\text{-}BrC_6H_4N_2BF_4$, 0.6 mmol of Me_4Sn, 0.05 mmol of a palladium catalyst, and dodecane (internal standard) in a 5-mL thermostated cell (25.4 °C) equipped with a side arm and a serum cap. Gas evolution was measured by a gas buret connected to the side arm. Samples were withdrawn at appropriate time intervals by a microsyringe and directly analyzed by GLC (silicone SE-30).

Registry No. $4\text{-}BrC_6H_4N_2^+Cl^-$, 2028-85-5; $4\text{-}BrC_6H_4N_2^+BF_4^-$, 673-40-5; $4\text{-}BrC_6H_4N_2^+PF_6^-$, 20566-57-8; $PhN_2^+BF_4^-$, 369-57-3; $2\text{-}MeC_6H_4N_2^+BF_4^-$, 2093-46-1; $3\text{-}MeC_6H_4N_2^+BF_4^-$, 1422-76-0; $4\text{-}MeC_6H_4N_2^+BF_4^-$, 459-44-9; $2\text{-}ClC_6H_4N_2^+BF_4^-$, 1956-97-4; $3\text{-}ClC_6H_4N_2^+BF_4^-$, 456-39-3; $4\text{-}ClC_6H_4N_2^+BF_4^-$, 673-41-6; $2\text{-}NO_2C_6H_4N_2^+PF_6^-$, 836-70-4; $3\text{-}NO_2C_6H_4N_2^+PF_6^-$, 1514-51-8; $4\text{-}NO_2C_6H_4N_2^+PF_6^-$, 1514-52-9; $4\text{-}NO_2C_6H_4N_2^+BF_4^-$, 456-27-9; $4\text{-}BrC_6H_4Me$, 106-38-7; PhMe, 108-88-3; $3\text{-}MeC_6H_4Me$, 108-38-3; $4\text{-}MeC_6H_4Me$, 106-42-3; $2\text{-}ClC_6H_4Me$, 95-49-8; $3\text{-}ClC_6H_4Me$, 108-41-8; $4\text{-}ClC_6H_4Me$, 106-43-4; $2\text{-}NO_2C_6H_4Me$, 88-72-2; $3\text{-}NO_2C_6H_4Me$, 99-08-1; $4\text{-}NO_2C_6H_4Me$, 99-99-0; $PhCH{=}CH_2$, 100-42-5; $4\text{-}MeC_6H_4Ph$, 644-08-6; Me_4Sn, 594-27-4; $CH_2{=}CHSnBu_3$, 7486-35-3; Ph_4Sn, 595-90-4; $PhSnBu_3$, 960-16-7; $Pd(OAc)_2$, 3375-31-3; $Pd(OCOCF_3)_2$, 42196-31-6; $Pd(dba)_2$, 32005-36-0.

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Organic Chemistry by Infrared Lasers. 4.[1] Laser-Induced Reactions of γ-Unsaturated Alcohols

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The laser-induced chemistry of 3-buten-1-ol (**1**), 3-butyn-1-ol (**2**), 3,4-pentadien-1-ol (**3**), 2-isopropenyl-5-methylcyclohexanol (*l*-isopulegol; **4**), and 1,5-hexadien-3-ol (**5**) is described. Retro-ene reactions occur in all cases, though with compound **5** a competitive oxy-Cope reaction is also observed. The reactions are generally clean and give rise to conversions in the range of 48–78% after 300–500 pulses. In these reactions between 2–10 photons are absorbed per molecule per pulse, and in some instances as much as 40% conversion is obtained after five pulses. The laser-induced chemistry seems to follow the known thermal chemistries of these systems.

γ-Unsaturated alcohols have received much attention in connection with thermolytic studies. These investigations originated with the liquid-phase pyrolysis of castor oil from which ricinoleic acid can be derived.[3] From this early research it was demonstrated that, depending upon the structure of the γ-unsaturated alcohols, a variety of gas-phase reactions can be accomplished. Representative examples of these reactions are illustrated in eq 1–3 and depict, respectively, a pyrolytic cleavage to olefin and carbonyl fragment,[4,5] an oxy-Cope rearrangement,[6] and a dehydrative cyclization.[7] Equation 1 is an example of the retro-ene fragmentation. This reaction has been studied

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