Addition of methanolic solutions of 1[2] or **3d** to 0.5–2 M aqueous sodium hydroxide gave solutions of the dianion of **3a**: UV λ_{max} 257 nm [lit.[9,10] λ_{max} 258 or 255 nm (ϵ 13 300 or 14 300)]; ^{13}C NMR (D_2O/NaOD) δ 21.9, 127.7, 128.9, 129.9, 142.6, 176.7, 178.3. After acidification of such solutions with hydrochloric acid at 0 °C, concentration and filtration gave **2a** in practically quantitative yield: mp 177–179 °C (lit.[4] mp 178 °C); IR spectrum as reported.[33]

Methanolysis of 4-Methyl-2,7-oxepindione (1). The cyclic anhydride[2] was dissolved in 100–200 parts by weight of methanol at room temperature. At various stages of the reaction (e.g. after 0.5, 1, 2, 5 h) a sample was evaporated and the residue examined by ^1H NMR spectroscopy ($CDCl_3$). After 1–2 h the product consisted largely of **3b** and **3c** together with an initially negligible but increasing amount of **2b** [δ 3.77 (methyl ester), 6.18 (H5), 8.53 (H4); ^3J_E = 16 Hz;[36] the remaining signals were overlapped by signals of major components], **4b**, and **5b**. Heating the mixture consisting of **3b** and **3c** in an oil bath (ca. 200 °C) for a few minutes and separation by column chromatography on silica gel with ether as the eluant gave the oily lactones **4b** and **5b**, which showed IR and ^1H NMR spectroscopic properties in close agreement with the literature.[33] Methylation of the mixture of **3b** and **3c** with ethereal diazomethane yielded **3d**.

(36) Cf.: Pattenden, G.; Weedon, B. C. L. *J. Chem. Soc. C* **1968**, 1984.

Acknowledgment. We thank Dr. K. Schaumburg (Chemical Laboratory V, University of Copenhagen) for ^1H NMR spectra recorded on a Bruker HX-270S spectrometer belonging to the Danish Natural Science Research Council and the Council for a fellowship to J.W.J.

Registry No. 1, 80533-00-2; **2a**, 31659-59-3; **2b**, 3555-79-1; **2d**, 80533-03-5; **3a**·2Na, 80533-04-6; **3b**, 80533-05-7; **3c**, 80533-06-8; **3d**, 61413-56-7; **4b**, 31656-70-9; **5b**, 31656-71-0; **6**, 80533-07-9; 4-methyl-1,2-benzoquinone, 3131-54-2; 4-methylcatechol, 452-86-8.

Acylative Cleavage of Ethers Catalyzed by Triorganotin Halides and Palladium(II) Complexes

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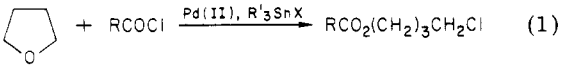
Benzylic, allylic, and cyclic ethers react with acyl halides under mild conditions in the presence of triorganotin halide and palladium(II) catalysts to give the corresponding esters in good yields. In the case of benzyl ether the other product is the benzyl halide, while in the reaction of allylic ethers the other products are various olefins resulting from the cleavage of the allyl group and an organotin moiety. The reaction is selective to these ethers, while acyclic aliphatic and phenolic ethers are unreactive. By control of the reaction conditions, benzylic and cyclic ethers could be cleaved in the presence of allylic ethers. The utility of the reaction as a deprotective method is demonstrated by the cleavage of a benzylic ether containing olefinic unsaturation. The mechanism of the benzylic and allylic ethers cleavage was studied by carrying out the corresponding stoichiometric reactions with the various palladium(II) complexes proposed in the catalytic cycle.

Introduction

Ethers are commonly used as blocking groups for the protection of hydroxylic functions; aliphatic, benzylic, and allylic ethers are used, among others, for this purpose.[2] The utility of ethers as protective groups depends on the susceptibility of the ether to facile removal by a specific reagent (that will not react with other functional groups present in the molecule). Some new reagents for selective ether cleavage have been reported recently[3a-f] (e.g., boron trifluoride etherate/mercaptoethanol,[3a] selenium dioxide/acetic acid,[3b] 1,2-bis[(trimethylsilyl)thio]ethane/zinc iodide/tetra-*n*-butylammonium iodide,[3c] and trimethylsilyl iodide[3d]). We here report a novel palladium-catalyzed cleavage of cyclic, allylic, and benzylic ethers is useful as a deprotection reaction for ethers but has no effect on other types of ethers (e.g., aliphatic, phenolic). A variety of other functional groups (including olefins, ketones, benzyl halides, and esters) that are sensitive to reductive or acidic cleavage procedures can be present in the reaction mixture.

Results and Discussion

Five-membered ring ethers can be cleaved and acylated in the presence of acyl halide, a catalytic amount of palladium(II) complex, and trialkyltin halide (eq 1) under mild conditions (Table I, entries 6, 8, 9), while almost no cleavage was detected with aliphatic and phenolic ethers (Table I, entries 1–4). The presence of a catalytic amount



(1)

of trialkyltin halide enhances the acylation although a slow reaction is detected even in the absence of the tin compound (Table I, entry 10). This selectivity is in contrast to that reported[4] for the acylation of aliphatic ethers catalyzed by acidic metal carbonyls of group 6 transition metals; in this case aliphatic ethers are readily cleaved. The interaction of the palladium catalyst with cyclic ethers is of interest since tetrahydrofuran is often used as a solvent in stoichiometric and catalytic reactions of palladium on the assumption that it is unreactive.

Strained cyclic ethers, including tetrahydrofuran, are known to be cleaved[5a-c] and to undergo cationic polym-

(1) Present address: Radiochemistry Department, Nuclear Research Centre-Negev, P. O. Box 9001, Beer-Sheva, Israel.

(2) See (a) Flowers, H. M. In "Chemistry of the Hydroxyl Group"; Patia, S., Ed.; Interscience: New York, 1969; Chapter 7, p 1001 and references therein. (b) Cunningham, J.; Gigg, R.; Warren, G. D. *Tetrahedron Lett.* **1964**, 1196. (c) Tate, M. E.; Bishop, C. D. *Can. J. Chem.* **1963**, *41*, 1801.

(3) See (a) Fujii, K.; Ichikawa, K.; Node, M.; Fuj, E. *J. Org. Chem.* **1979**, *44*, 1661. (b) Harrison, I. T.; Harrison, S. In "Compendium of Organic Method"; Wiley-Interscience: New York, 1971; Vol. 1, pp 92–99, 127–128. (c) Hanessian, S.; Guidon, Y. *Tetrahedron Lett.* **1980**, 2305. (d) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761. (e) Spyroudis, S. S.; Varvoglis, A. *J. Chem. Soc., Chem. Commun.* **1979**, 615. (f) Naraganan, C. R.; Iger, K, N. *J. Org. Chem.* **1965**, *30*, 1734.

(4) Alper, H.; Huang, C.-C. *J. Org. Chem.* **1973**, *38*, 64.

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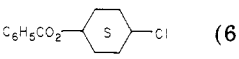
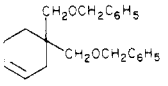
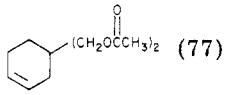
Table I. Acylative Cleavage of Aliphatic Ethers Catalyzed by Palladium(II) Complex[a]

entry	ether	palladium catalysts, mol %	$(n\text{-}C_4H_9)_3SnCl$, mol %	product (% yield)[b]
1	$(n\text{-}C_4H_9)_2O$	0.6	15	no reaction
2	$(C_6H_5)_2CHOC_2H_5$	0.6	15	$C_6H_5CO_2C_2H_5$ (10)
3	$(CH_3)_3COC_2H_5$	0.6	15	$C_6H_5CO_2C_2H_5$ (8)
4	$CH_3OC_6H_5$	0.6	15	no reaction
5		0.3	50	$CH_3CO_2(CH_2)_3CH_2Cl$ (95)[c]
6		0.4	15	$C_6H_5CO_2(CH_2)_3CH_2Cl$ (85)
7		0.5	15	$C_6H_5CO_2(CH_2)_4CH_2Cl$ (4)
8		0.5	15	$C_6H_5CO_2(CH_2)_3CH(CH_3)Cl$ (81)
9		0.7	15	 (60)
10		0.7		$C_6H_5CO_2(CH_2)_3CH_2Cl$ (30)

[a] All reactions were performed at 63 °C for 48 h with benzylchlorobis(triphenylphosphine)palladium(II) as catalyst and benzoyl chloride as acylating agent except where noted by *c*. [b] Products were isolated and identified by their ^1H and ^{13}C NMR spectra. [c] Acetyl chloride was used as an acylating agent.

Table II. Acylative Cleavage of Benzylic Ethers by Acetyl Chloride Catalyzed by Palladium(II)[a]

entry	ether	palladium(II)[b] catalyst (mol %)	triorganotin[c] halide (mol %)	product (% yield)[d]
1	$C_6H_5CH_2OCH_3$	1 (0.6)	2 (10)	$C_6H_5CH_2Cl$ (89) $CH_3CO_2CH_3$ (95)
2	$(C_6H_5CH_2)_2O$	1 (0.6)	2 (10)	$C_6H_5CH_2Cl$ (80) $C_6H_5CH_2OCOCH_3$ (88)
3	$(C_6H_5CH_2)_2O$	1 (0.6)	3 (50)	$C_6H_5CH_2Cl$ (69) $C_6H_5CH_2OCOCH_3$ (76)
4	$C_6H_5CH_2OCH_3$	1 (0.6)	4 (50)	$C_6H_5CH_2Cl$ (45) $C_6H_5CH_2Br$ (45) CH_3OCOCH_3 (98)
5	$C_6H_5CH_2OCH_3$	5 (0.1)	2 (10)	CH_3OCOCH_3 (70) $C_6H_5CH_2Cl$ (77)[e] $C_6H_5CH_2Cl$ (70)
6		1 (0.6)	2 (10)	 (77)

[a] Reactions carried out at 63 °C for 48 h. [b] 1, $PhCH_2PdCl(PPh_3)_2$; 5, $PhCOPdCl(PPh_3)_2$. [c] 2, $n\text{-}Bu_3SnCl$; 3, Me_3SnCl; 4, Me_3SnBr. [d] Product isolated and identified by ^1H and ^{13}C NMR spectra; yields based on NMR or GC. Traces of biphenyl (~5%) were detected as a result of coupling of benzyl halide.

erization[5d] catalyzed by Lewis acids, but weak Lewis acids such as tri-*n*-butyltin chloride and trimethyltin chloride failed to induce acylation in tetrahydrofuran unless a catalytic amount of palladium(II) compound was introduced into the mixture. Oxiranes are acylated without a catalyst, while tetrahydropyran is much less reactive than tetrahydrofuran (Table I, entries 6, 7). The reaction of 2-methyltetrahydrofuran gave predominately 4-chloro-4-methylbutyl benzoate (Table I, entry 8), suggesting an S_N1 ring-opening process, analogous to its cleavage by zinc chloride.[6]

In reactions of benzyl and allyl ethers, the cleavage is selective to the benzylic oxygen or allylic oxygen bond, producing the debenzylated or deallylated esters. The scope of the cleavage reactions of benzylic ethers (eq 2) is shown in Table II. This reaction is of practical value

$$C_6H_5CH_2OR + R'COCl \xrightarrow{Pd(II),\ R''_3SnX} C_6H_5CH_2X + R'CO_2R \quad (2)$$

in cases where the usual reductive cleavage of benzylic ether is unsuitable.[7] Cleavage of 1,1-bis[(benzyloxy)-methyl]cyclohex-3-ene is an example of a benzyl ether containing an olefinic group (Table II, entry 6).

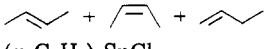
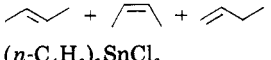
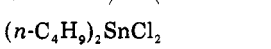
While the cleavage using a 1:1 molar ratio of benzyl ether and acyl halide gave fair yields of ester, a large excess of the acyl halide slowed the rate of benzyl ether cleavage and lower conversions were obtained. The benzyl ether cleavage was also found to be retarded by addition of small amounts of triphenylphoshine or by using tetrakis(triphenylphosphine)palladium(0) as the catalyst.

(5) (a) Johnson, F. In "Friedel Crafts Alkylations and Related reactions"; Olah, G. A., Ed.; Wiley-Interscience: New York, 1965, Vol. 4, pp 1277. (b) Burwell, R. T., Jr. *Chem. Rev.* **1954**, *54*, 615. (c) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; p 1141. (d) Cationic polymerization of cyclic ethers is also restricted to strained rings including tetrahydrofuran: Lenz, R. W. In "Organic Chemistry of Synthetic High Polymers"; Interscience: New York, 1967; pp 532-534.

(6) Garania, D.; Butt, *A. Bull. Soc. Chim. Fr.* **1960**, 309.

(7) The usual methods for removal of a benzyl protective group are as follows: catalytic hydrogenolysis,[8] reductive cleavage with sodium in ethanol of liquid ammonia,[9] or various techniques of hydrogen transfer.[10]

Table III. Acylative Cleavage of Allylic Ethers and Esters Catalyzed by Palladium(II) Complexes[a]

entry	ether	trialkyltin[b] halide (mol %)	palladium(II)[c] catalyst (mol %)	products[d] (% yield)	
1	$C_6H_5OCH_2CH=CH_2$	2 (20)	1 (0.7)	$CH_3CO_2C_6H_5$	(15)
				$(n\text{-}C_4H_9)_2SnCl_2$	(20)
2	$C_6H_5OCH_2CH=CH_2$	2 (90)	1 (0.7)	$CH_3CO_2C_6H_5$	(73)
				$CH_2=CHCH_3$	(45)
				$(n\text{-}C_4H_9)_2SnCl_2$	(75)
					(65)
3	$C_6H_5OCH_2CH=CH_2$	3 (100)	1 (0.7)	no reaction	
4	$CH_3CO_2CH_2CH=CH_2$	2 (100)	1 (0.5)	$(CH_3CO)_2O$	(45)
				$CH_3CH=CH_2$	(15)
					(30)
				$(n\text{-}C_4H_9)_2SnCl_2$	(50)
5	$C_6H_5OCH_2CH=CH_2$	2 (100)	4 (0.5)	$CH_3CO_2C_6H_5$	(82)
				$CH_3CH=CH_2$	(55)
					(72)
				$(n\text{-}C_4H_9)_2SnCl_2$	(82)
6	$C_6H_5OCH_2CH=CH_2$[e]	2 (100)	5 (0.7)	$CH_3CO_2C_6H_5$	(62)
				$CH_3CH=CH_2$	(f)
					(f)
				$(n\text{-}C_4H_9)_2SnCl_2$	(85)
7	$n\text{-}C_6H_{13}OCH_2CH=CH_2$	2 (100)	1 (0.7)	$CH_3CO_2(n\text{-}C_6H_{13})$	(81)
				$CH_3CH=CH_2$	(f)
					(f)
				$(n\text{-}C_4H_9)_2SnCl_2$	(85)

[a] Reactions were conducted at 63 °C for 48 h with acetyl chloride as acylating agent except where noted by *e*. [b] 2, $(n\text{-}C_4H_9)_3SnCl$; 3, $(CH_3)_3SnCl$. [c] 1, $PhCH_2PdCl(PPh_3)_2$; 4, $PhCOPdCl(PPh_3)_2$; 5, $[(\pi\text{-}C_3H_5)_2PdCl]_2 + 2PPh_3$. [d] Products were isolated and identified by ^1H and ^{13}C NMR; yields were determined by ^1H NMR and GC. Olefins were characterized in the mixture by IR, ^1H NMR, and ^{13}C NMR and their yields were determined by GC of the corresponding dibromides obtained by addition of bromine in the mixture. [e] Reaction time, 24 h; acylating agent, acetyl chloride. [f] Identified but not determined quantitatively.

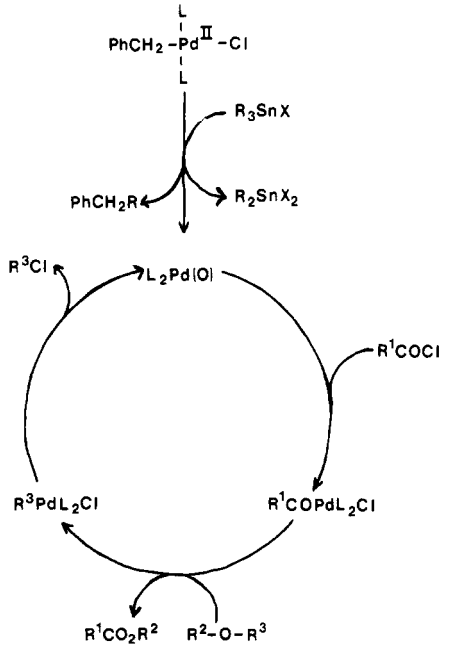
The palladium-catalyzed coupling reaction of tetraalkyltin reagent with acid chloride has been demonstrated[11] to give high yields of ketones. Consequently, tetraalkyltin reagents were avoided in the ether cleavage reaction, and tributyltin chloride, which only very slowly produces ketones by coupling with the acid chloride, was used as a cocatalyst.

The reaction of allylic ethers, however, is stoichiometric with respect to the tributyltin halide, and the products, in addition to the deallylated ester, are propene and a mixture of butenes, originating from the allylic group of the ether and the butyl groups of the tributyltin chloride, respectively (eq 3).

$$(n\text{-}C_4H_9)_3SnCl + CH_3COCl + C_6H_5OCH_2CH{=}CH_2 \xrightarrow{Pd(II)} (n\text{-}C_4H_9)_2SnCl_2 + CH_3CO_2C_6H_5 + CH_2{=}CHCH_3 + C_4H_8 \quad (3)$$

The reaction does not take place when trimethyltin chloride was used as the tin compound (Table III, entry 3). The reaction is also applicable to allylic esters, but the conversion is lower (Table III, entry 4). An alkyl allyl ether (*n*-hexyl allyl ether) was as reactive as the phenyl allyl ether (Table III, entry 7). Like the alkyl and benzyl ether cleavages, the allylic ethers cleavage is retarded by addition of small amounts of triphenylphosphine.

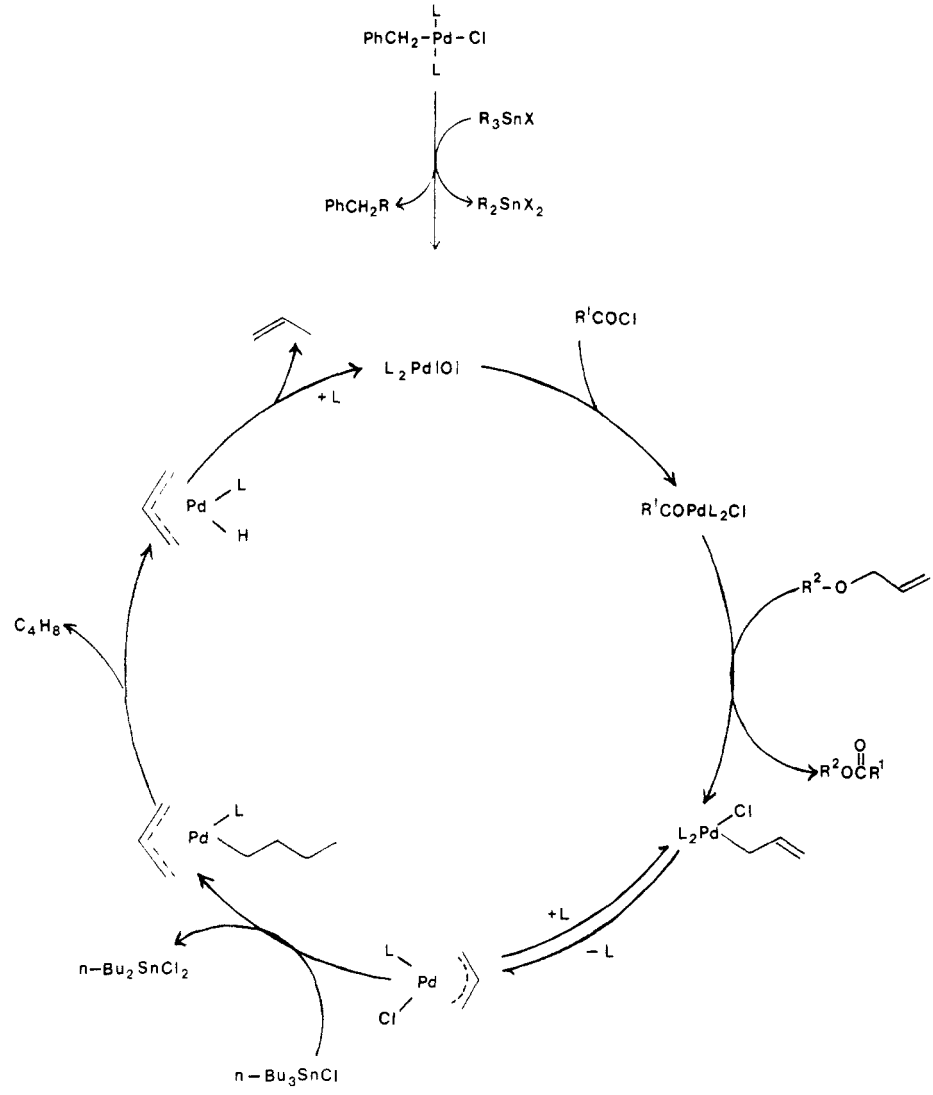
Scheme I. Catalytic Cycle for Benzyl and Cyclic Ethers Acylative Cleavage



The most consistent mechanism for the cleavage of benzylic and cyclic ether is shown in Scheme I. The following experimental facts support this mechanism. The implication of a benzoylpalladium species in the catalytic cycles was demonstrated by the fact that benzylchlorobis(triphenylphosphine)palladium(II) was an effective

(8) Raylander, P. N. In "Catalytic Hydrogenation over Platinum Metals"; Academic Press: New York, 1967; p 449.
(9) Barton, D. H.; Magnes, P. D.; Srecket, G. S.; Furr, D. *J. Chem. Soc., Perkin Trans. 1* **1972**, 542.
(10) Olah, G. A.; Surya-Parkash, G. K.; Narang, C. *Synthesis* **1978**, 11, 825.
(11) Milstein, D.; Stille, J. K. *J. Org. Chem.* **1979**, *44*, 1613.

Scheme II. Catalytic Cycle for Allyl Ethers Acylative Cleavage



catalyst for the benzyl ether cleavage (Table II, entry 5). Such a benzylpalladium species was shown to be formed by the oxidative addition of an acyl halide to a palladium(0) complex.[11] (The palladium(0) complex is formed from the starting palladium(II) by reduction with the tin compound.)

Inhibition of the reaction by the addition of small amounts of triphenylphosphine further supports the acyl halide oxidative addition step in the catalytic cycle, since phosphine is known[12] to retard such oxidative addition reactions. The slower reaction rate in the presence of a large excess of acyl halide could be the result of a competitive decarbonylation of the acylpalladium intermediate to give decarbonylated coupling products with the acyl halide. Indeed, this reaction (eq 4) was found to be the dominate process when benzoylchlorobis(triphenylphosphine)palladium(II) was heated in a large excess of benzoyl chloride.

$$PhCOPdCl(PPh_3)_2 + PhCOCl \rightarrow PhCOPh + PdCl_2(PPh_3)_2 \quad (4)$$

The nucleophilic attack of the ether on the acylpalladium intermediate seems to be restricted to strained five-membered-ring ethers or reactive benzylic ethers. The details of this nucleophilic attack are not known although such an attack is considered to be a step in the carbonylation of organohalides by transition metals where nucleophiles such as alcohols and amines are used.[13] The mode of cleavage of 2-methyltetrahydrofuran supports an S_N1 mechanism for this case.

The mechanism of the acylative cleavage of allylic ethers differs from that of the platinum-metal-assisted allylic ether cleavage[14] in which π-allyl association[14a] or oxidative addition of the ether[14b] was proposed. A mechanism which accounts for the unusual features of this reaction is given in Scheme II. The following experimental facts support this mechanism. The presence of the benzoylpalladium species in this catalytic cycle was established by the effectiveness of benzoylchlorobis(triphenylphosphine)palladium(II) as a catalyst (Table III, entry 5) and by its fast stoichiometric reaction with allyl phenyl ether (eq 5) to give 85% yield of phenyl benzoate after a 4-h reaction at 63 °C.

$$PhCOPdCl(PPh_3)_2 + PhOCH_2CH{=}CH_2 \rightarrow PhCO_2Ph + [CH_2{=}CHCH_2PdCl(PPh_3)_2] \quad (5)$$

The palladium product was not identified due to its rapid decomposition once the solvent was removed. The

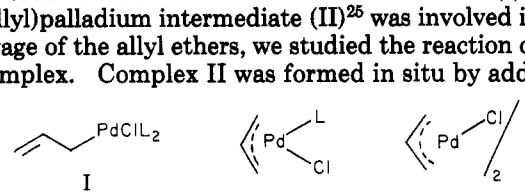
(12) See Tolman, C. A. *Chem. Rev.* **1977**, *77*, 13 and references therein.

(13) Heck, R. F. *Pure Appl. Chem.* **1978**, *50*, 691.

(14) (a) Corey, E. J.; Suggs, W. *J. Org. Chem.* **1973**, *38*, 3224. (b) Takahashi, T.; Miyake, A.; Hata, G. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 230. (c) Eisch, J. J.; Im, K. R. *J. Organomet. Chem.* **1977**, *139*, C45.

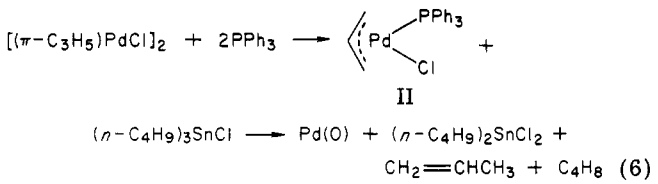
formation of a benzoylpalladium intermediate by an oxidative addition of acyl halide to a palladium(0) complex was inhibited by addition of small amounts of triphenylphosphine.

In order to determine whether a σ-bonded (I) or a (η^3-allyl)palladium intermediate (II)[25] was involved in the cleavage of the allyl ethers, we studied the reaction of the η^3 complex. Complex II was formed in situ by addition



I II III

of triphenylphosphine to a solution of (π-allyl)palladium chloride dimer.[15] Stepwise addition of triphenylphosphine causes the two doublets (4.10, 3.04 ppm) in the ^{1}H NMR of the symmetric π-allyl dimeric complexes to collapse gradually into one doublet (3.83 ppm) after the addition of 4 mol equiv of the phosphine to the dimer. Tributyl chloride was more reactive toward the (η^3-allyl)palladium complex (II; obtained after the addition of 2 mol equiv of phosphine) than toward the π-allyl dimer (III) or the σ-allyl complex (I). When 2 equiv of phosphine was added to the (π-allyl)palladium dimer, the reaction with tributyltin chloride (eq 6) took place immediately and reduced metal precipitated after a few seconds of heating to 63 °C; 93%



of di-*n*-butyltin dichloride was isolated after a 30-min reaction. The other products were the same olefins obtained in the catalytic allyl ether cleavage. On the other hand, no reaction of tributyltin chloride took place when 4 mol equiv of triphenylphosphine was added to the (π-allyl)palladium chloride dimer to form the (σ-allyl)palladium complex (I). Tributyltin chloride was quantitatively recovered after heating 48 h at 63 °C with I. These results support the formation of η^3 complex II as an intermediate in the catalytic cycle. The free phosphine which is formed together with the η^3 complex II is consumed later in the catalytic cycle to reproduce the starting palladium(0) catalyst. It would be also in equilibrium with the corresponding phosphonium salt formed by reaction with the acyl halide[17] and thus not reacting back with the η^3 complex II.

While the oxidative addition of allyl ether to palladium(0) is known for phenyl allyl ether,[14b], it was shown[16] that alkyl ethers are unreactive under the same conditions. Thus, the fact that *n*-hexyl allyl ether was found to be as reactive as the phenyl allyl ether (Table III, entries 2, 7) supports a mechanism in which oxidative addition of the allyl ether is not playing any important rule. Instead its nucleophilic attack on the benzoylpalladium complex probably is taking place. A (π-allyl)butylpalladium intermediate is suggested to be formed by the metathesis reaction of tributyltin chloride and (η^3-allyl)palladium(II). Only little 1,1-reductive elimination of this relatively stable (π-allyl)butylpalladium occurs. However, its existence is supported by the traces of heptene (2–3%) found in the catalyzed allyl ether cleavage reactions. β-Hydrogen elimination from the σ-butyl group takes place readily in this 16-electron π-allyl complex[18] to give butene and the allylpalladium hydride. The lack of reactivity of trimethyltin chloride (Table III, entry 3) is evident, then, since a β-elimination pathway is not available and the π-allyl–σ-methyl complex is relatively stable.

Carrying out the reaction shown in eq 6 but replacing tributyltin chloride with tetramethyltin gave a 60% of trimethyltin chloride after a 6-h reaction, but no palladium precipitated, and the resulting (π-allyl)palladium complex remained in the solution as indicated by its ^{1}H NMR spectrum. A new signal at 0.20 ppm could be attributed to a methylpalladium complex. Unfortunately, attempts to isolate and identify this π-allyl complex failed due to its rapid decomposition once the solvent was removed.

Experimental Section

The reactions were carried out with a Schlenck apparatus under an atmosphere of argon. ^{1}H NMR spectra were taken on a Varian EM 360 spectrometer and ^{13}C NMR spectra were obtained on a JEOL FX-100 spectrometer. IR spectra were taken on a Beckman IR 4240 instrument. GC separations were performed on a Varian Aerograph 1520 on a 20% SE30/Chromosorb W (60–80 mesh) 0.25 in. × 10 ft column. Preparative TLC was carried out on precoated silica gel F-254 plates. Commercial ethers and solvents were distilled and degassed before use. The acid chlorides were heated to reflux with phosphorus pentoxide (acetyl chloride) or thionyl chloride (benzoyl chloride) and then distilled. The catalysts tetrakis(triphenylphosphine)palladium(0),[19] benzylchlorobis(triphenylphosphine)-palladium(II),[20] benzoylchlorobis(triphenylphosphine)palladium(II),[22] and (π-allyl)palladium chloride dimer[21] were prepared by known procedures.

Acylative Cleavage of Tetrahydrofuran. To a mixture of 550 mg (7.00 mmol) of acetyl chloride, 330 mg (1.01 mmol) of tributyltin chloride, and 505 mg (7.00 mmol) of tetrahydrofuran was added 35.0 mg (0.049 mmol) of chlorobenzylbis(triphenylphosphine)palladium(II). The mixture was heated to 63 °C in a capped reaction vessel for 48 h, during which time the color changed from yellow to black. The volatile fractions were transferred by means of a reduced pressure distillation to a cold trap at −180 °C. The nonvolatile residue was dissolved in ether and extracted with saturated sodium bicarbonate and potassium fluoride aqueous solutions. The ether layer was dried ($MgSO_4$) and filtered and the ether was evaporated to leave almost pure (4-chlorobutyl)acetate which was further purified by a preparative TLC with hexene/ethyl acetate (10:1; R_f 0.6) to give 990 mg (95%) of (4-chlorobutyl)acetate, whose spectrum was identical with that reported:[4] IR ($CDCl_3$) ν 1740 (carbonyl) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.01 (t, J = 6 Hz, 2, CH_2OAc), 3.57 (t, J = 6 Hz, 2, CH_2Cl), 2.10 (s, 3, CH_3CO), 2.05–1.79 (m, 4, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 170.53 (carbonyl), 63.51 (CH_2Cl), 44.30 (CH_2OAc), 29.36 (CH_2), 26.32 (CH_2), 20.83 (CH_3).

4–Chlorobutyl benzoate was similarly obtained from the reaction with benzoyl chloride and was purified by TLC (R_f 0.5) to give 1.26 g (86%) yield of 4-chlorobutyl benzoate, whose spectrum was identical with that reported:[23] ^{1}H NMR ($CDCl_3$) δ 8.16–7.75, 7.48–7.20 (m, 5, C_6H_5), 4.34 (t, J = 6 Hz, 2, CH_2-COPh), 3.59 (t, J = 6 Hz, 2 CH_2Cl), 1.92 (m, 4, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 166.11 (carbonyl) 135.28, 129.27, 128.39, 128.10 (C_6H_5), 63.93 (CH_2Cl), 44.37 (CH_2OAc), 29.25 (CH_2), 26.16 (CH_2).

Acylative Cleavage of 2-Methyltetrahydrofuran. A mixture of 2-methyltetrahydrofuran (603 mg, 7.00 mmol), benzoyl chloride (984 mg, 7.00 mmol), tributyltin chloride (330 mg, 1.01

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mmol), and chlorobenzylbis(triphenylphosphine)palladium(II) (35 mg, 0.049 mmol) was heated to 63 °C for 48 h. The reaction mixture worked up as described for the tetrahydrofuran reaction to give 1.193 g (81% yield) of 4-chloropentyl benzoate, whose spectrum was identical with that reported:[4] ^{1}H NMR ($CDCl_3$) δ 8.06–7.73, 7.48–7.12 (m, 5, C_6H_5CO), 4.32–4.08 (m, 3, $OCOCH_3$), 2.06–1.65 (m, 4, CH_2CH_2), 1.45 (d, J = 7 Hz, 3, CH_3CCl).

Acylative Cleavage of 7-Oxabicyclo[2.2.1]heptane. A mixture of 7-oxabicyclo[2.2.1]heptane (687 mg, 7.00 mmol), benzoyl chloride (984 mg, 7.00 mmol), tributyltin chloride (330 mg, 1.01 mmol), and chlorobenzylbis(triphenylphosphine)palladium(II) (35 mg, 0.049 mmol) was heated to 63 °C for 48 h. The reaction mixture worked up as described for the tetrahydrofuran reaction to give 1.01 g (60% yield) of *trans*-4-chlorocyclohexyl benzoate, whose spectrum was identical with that reported:[4] IR ($CDCl_3$) ν 1712 (carbonyl) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.03–7.64, 7.40–7.02 (m, 5, C_6H_5CO), 5.14–4.73 (m, 1, CHOCO), 4.21–3.80 (m, 1, CHCl), 2.51–1.50 (m, 8, methylenes).

Acylative Cleavage of Benzyl Ethers. The cleavage reactions of various benzyl ethers was carried out as described for tetrahydrofuran. A representative example is the reaction of benzyl methyl ether (854 mg, 6.99 mmol) and acetyl chloride (550 mg, 7.00 mmol). The yields of products in the volatile fraction containing residual acetyl chloride (16.0 mg, 3%) and methyl acetate (492 mg, 95%) were determined by ^{1}H NMR with dichloromethane as internal standard. The nonvolatile residue contained 780 mg (89%) of benzyl chloride and traces of palladium residue.

Acylative Cleavage of 1,1-Bis[(benzyloxy)methyl]cyclohex-3-ene. The reaction of 2.25 g (6.96 mmol) of 1,1-bis[(benzyloxy)methyl]cyclohex-3-ene [prepared by refluxing benzyl bromide and 1,1-bis(hydroxymethyl)cyclohex-3-ene disodium in benzene solution for 4 h with acetyl chloride (550 mg, 7.00 mmol)] gave 611 mg (70%) of benzyl chloride and 1,1-bis(acetoxymethyl)cyclohex-3-ene (1.22 g, 77% yield), whose spectrum was identical with that reported:[24] ^{1}H NMR ($CDCl_3$) δ 5.63 (br s, 2, CH=CH), 3.90 (s, 4, CH_2O), 2.05 (s, 6, CH_3CO), 2.05–1.40 (m, 6, methylenes).

Acylative Cleavage of Allyl Phenyl Ether. The reaction was carried out as in the acylation of tetrahydrofuran except a stoichiometric amount of tributyltin chloride was added. The reaction mixture was worked up as outlined for the tetrahydrofuran reaction. The volatile fraction of the reaction mixture was distilled at reduced pressure [25 °C (0.1 mm)] and its NMR spectra were recorded. A molar equivalent amount of bromine was added to the cooled (−50 °C) solution, and the mixture was allowed to warm to 25 °C and was then stirred for another hour. The resulting dibromides were identified and their yields were determined by GC in comparison to authentic samples of commercially available dibromides.

Retention times (100 °C: 1,2-dibromopropane (4.5 min), 2,3-dibromobutane (6.5 min), 1,2-dibromobutane (7.8 min). ^{13}C NMR of the olefins mixture ($CDCl_3$): propene (δ 124.35, 112.90, 13.07), 1-butene (δ 133.52, 112.90, 26.85, 12.37), 2-butenes (δ 124.35, 125.63, 17.97). Dibutyltin dichloride (1.489 g 75%) was determined in the nonvolatile fraction, using GC (160 °C, t_R = 8.3 min). The nonvolatile fraction was then worked up with aqueous potassium fluoride solution to remove organotin chlorides as described for the tetrahydrofuran reaction and the yield of the residual phenyl acetate (690 mg, 73%) was determined by ^{1}H NMR, using dichloromethane as an internal standard.

Stoichiometric Reaction of Chlorobenzoylbis(triphenylphosphine)palladium(II) with Allyl Phenyl Ether. To a solution of 65.0 mg (0.500 mmol) of phenyl allyl ether in 2.5 mL of acetonitrile-d_3, kept under argon atmosphere, was added 340 mg (0.400 mmol) of chlorobenzoylbis(triphenylphosphine)palladium(II). The mixture was heated for 4 h at 63 °C in a capped reaction vessel. The palladium(II) complex went into solution as heating began and the color gradually changed from yellow to orange brown. The solvent was removed by reduced-pressure distillation and the nonvolatile residue was washed twice with 10-mL portions of *n*-hexane. The combined hexane washings were evaporated, and the white solid residue was found to be 67 mg (85% yield) of phenyl benzoate [IR ($CDCl_3$) ν 1735 (carbonyl) cm^{-1}]. The hexane-washed yellow palladium complex was kept under argon; however, rapid color change to brown black indicated the decomposition of this product. This partially decomposed product showed no carbonyl absorption in the IR spectrum, and only aromatic signals were found in its ^{1}H and ^{13}C NMR spectra.

Stoichiometric Reaction of (η^3-Allyl)palladium Complex with Tributyltin Chloride. To a solution of 40.0 mg (0.100 mol) of (π-allyl)palladium chloride dimer and 53.0 mg (0.200 mmol) of triphenylphosphine in 0.5 mL of chloroform-d_1 was added 53.0 mg (0.200 mmol) of tributyltin chloride. The color changed rapidly from yellow to red after a few seconds at room temperature. Heating of the mixture to 63 °C caused rapid blackening and metallic mirror precipitated after 2 min. The ^{1}H NMR signals assigned to the (π-allyl)palladium species disappeared after 30 min at 63 °C; instead, the signals of the free olefins were detected (this spectrum was identical with that of the olefin mixture formed in the cleavage of an allyl ether). The solvent and the olefin mixture were removed by reduced-pressure distillation, and the black residue was washed with two 10-mL portios of *n*-hexane. The combined hexane washings were then evaporated to give a mixture of 34 mg (85%) of phenyl benzoate, whose yield was determined by GC (200 °C, t_R = 2.8 min), and 56 mg (93%) of dibutyltin dichloride, whose yield was determined by GC (160 °C, t_R = 8.3 min). The black, hexane-washed residue was suspended in chloroform and was found to contain 34 mg (65%) of the starting triphenylphosphine (yield was determined by ^{1}H NMR); no carbonyl adsorption was detected in this fraction.

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Registry No. Ethyl benzoate, 93-89-0; 4-chlorobutyl acetate, 6962-92-1; 5-chloropentyl benzoate, 55092-47-2; 4-chloropentyl benzoate, 36978-17-3; *trans*-4-chlorocyclohexyl benzoate, 36978-28-6; 4-chlorobutyl benzoate, 946-02-1; benzyl chloride, 100-44-7; methyl acetate, 79-20-9; benzyl acetate, 140-11-4; benzyl bromide, 100-39-0; 1,1-bis(acetoxymethyl)cyclohex-3-ene, 27025-19-0; phenyl acetate, 122-79-2; dibutyltin dichloride, 683-18-1; propene, 115-07-1; (*E*)-2-butene, 624-64-6; (*Z*)-2-butene, 590-18-1; 1-butene, 106-98-9; acetic anhydride, 108-24-7; hexyl acetate, 142-92-7; 1,2-dibromopropane, 78-75-1; 2,3-dibromobutane, 5408-86-6; 1,2-dibromobutane, 533-98-2; butyl ether, 142-96-1; ethyl 1-ethylpropyl ether, 36749-13-0; *tert*-butyl ethyl ether, 637-92-3; methyl phenyl ether, 100-66-3; tetrahydrofuran, 109-99-9; tetrahydro-2*H*-pyran, 142-68-7; 2-methyltetrahydrofuran, 96-47-9; 7-oxabicyclo[2.2.1]heptane, 279-49-2; benzyl methyl ether, 538-86-3; benzyl ether, 103-50-4; 1,1-bis[(benzyloxy)methyl]cyclohex-3-ene, 80595-07-9; allyl phenyl ether, 1746-13-0; allyl hexyl ether, 3295-94-1; benzoyl chloride, 98-88-4; acetyl chloride, 75-36-5; (n-C_4H_9)$_3$SnCl, 1461-22-9; Me_3SnCl, 1066-45-1; Me_3SnBr, 1066-44-0; $PhCH_2PdCl(PPh_3)_2$, 22784-59-4; $PhCOPdCl(PPh_3)_2$, 50417-59-9.

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