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Reaction of Olefins with Palladium Trifluoroacetate

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Received September 28, 1979

Abstract: The reaction of palladium trifluoroacetate with acyclic olefins (including monosubstituted olefins) and some alkylidenecycloalkanes led in high yield to π-allylpalladium complexes. The chemo- and regioselectivity of the reaction were examined. Reactions of cyclohexenes led to disproportionation. A catalytic dehydrogenation to substituted benzenes evolved by use of maleic acid as a hydride acceptor. The mechanistic implications with respect to olefin vs. allylic oxidation and oxidation vs. π-allylpalladium formation are discussed.

Introduction

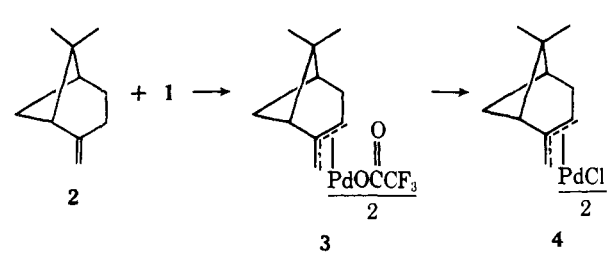
The reaction of olefins with palladium salts has been intensively studied as a result of its relevance to the important Wacker process.[1] For monosubstituted olefins, the major reaction is oxidation, normally to the methyl ketone.[1,2] For internal olefins, both oxidation of the olefin and at an allylic position are observed.[1,2] In these olefins, formation of π-allyl complexes sometimes can be accomplished by suitable modification of reaction conditions.[3-14] At this point, the factors which control the product (i.e., oxidation vs. π-allyl formation) remain obscure. Our recent interest[15] in the utilization of π-allylpalladium complexes in synthesis led us to explore this competition—especially in conjunction with our interest in generating a catalytic procedure for allylic alkylation.[16]

Palladium trifluoroacetate, first prepared by Wilkinson,[17] was unexplored in its reactions with organic substitutes. Such a salt has particular interest since, while it is strongly electrophilic, it possesses a nonbasic and relatively nonnucleophilic counterion. The oxidation of olefins appears to involve the attack of an oxygen nucleophile on an olefin–palladium complex,[2,18] whereas the formation of the π-allyl species has been thought to require a base.[5,7] The absence of both features in palladium trifluoroacetate makes its reactions with olefins especially instructive.

From a preparative point of view, we required an improved procedure for the synthesis of π-allylpalladium complexes. In our hands, the most general procedure involves the use of palladium chloride, cupric chloride, sodium chloride, and sodium acetate in a mixture of acetic anhydride and acetic acid at 60–90 °C.[11] The use of milder conditions and nonacidic solvents might improve the selectivity of the reaction and facilitate isolation. Most importantly, all methods for formation of such complexes involve an excess of olefin. While it is frequently recoverable, a procedure which allowed a 1:1 olefin:palladium salt ratio clearly is desirable. In this paper, we wish to report a method that fulfills these desires and to describe its limitations. We also report a particularly facile disproportionation of cyclohexenes.

Results

Palladium trifluoroacetate (**1**) is prepared by the reaction of commercially available palladium acetate with excess trifluoroacetic acid[17] or by conversion of palladium chloride to its oxide followed by treatment with trifluoroacetic acid at 80 °C.[19] The former procedure was generally preferred for convenience and better reproducibility. Dissolving β-pinene (**2**) in acetone-d_6 and adding palladium trifluoroacetate led, in the NMR spectrum, to rapid replacement of the olefin signals at δ 4.54 by a multiplet at δ 4.40 and broad singlets at δ 3.83 and 3.25 which correspond nicely to the signals of the π-allylpalladium complex **3**. Apparently at room temperature and in a



2 **3** **4**

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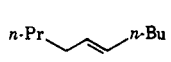
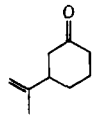
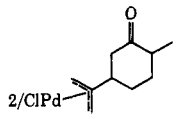
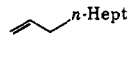
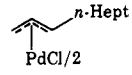
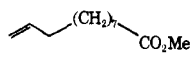
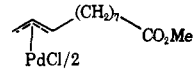
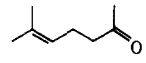
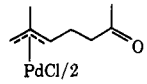
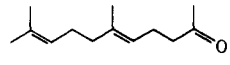
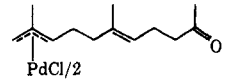
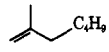
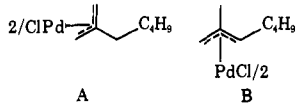
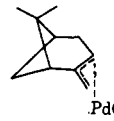
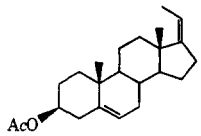
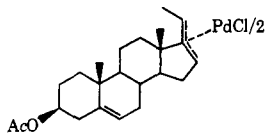
Table I. Preparation of π-Allylpalladium Chloride Complexes

entry	substrate	complex(es)	acetone	yields, %, in EtOAC	THF
1			70		
2			66[a]		
3			68	64	50
4			68	78	82
5			70		
6			83[b]		
7		 A B	80[c,d]		
8			83		
9			92[e]		

[a] Reaction time: overnight. [b] Starting material was recovered in 29% yield. The yield of complex given is based upon recovered starting material. [c] Reaction time: 3 h. [d] These isomers were not separated. NMR indicates a composition of 52% A and 48% B. [e] The material used contains an estimated 7% of the *E* isomer.

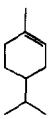
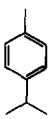
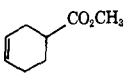
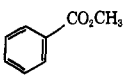
matter of minutes the olefin was surprisingly converted cleanly into its π-allyl complex with no other products detectable in the NMR spectrum. Verification of this interpretation was sought by a preparative experiment. Since initial attempts to isolate the trifluoroacetate complex led to substantial decomposition, we converted the trifluoroacetate to the chloride **4** by addition of tetra-*n*-butylammonium chloride to the reaction after complex formation was complete. Isolation gave the crystalline complex **4** in 83% yield.

Careful crystallization of the crude oil directly from the reaction allowed the trifluoroacetate complex **3** also to be isolated in 54% yield. The lower yield compared to the isolation of the chloride complex reflects the greater lability of the trifluoroacetates. There has been only one previous report of a trifluoroacetate which was made by an exchange reaction.[20] Thus, this represents the first direct method for their formation. While the composition is established by analysis, their dimeric nature is assumed based upon analogy to the corresponding acetates. It is interesting to note the considerable downfield shift of the ^{13}C NMR signal of the central carbon (δ 140.0) relative to the corresponding chlorides in analogous complexes (δ 120 ± 6).[21] For the purpose of preparing π-allylpalladium complexes, anion metathesis to the chlorides is recommended.

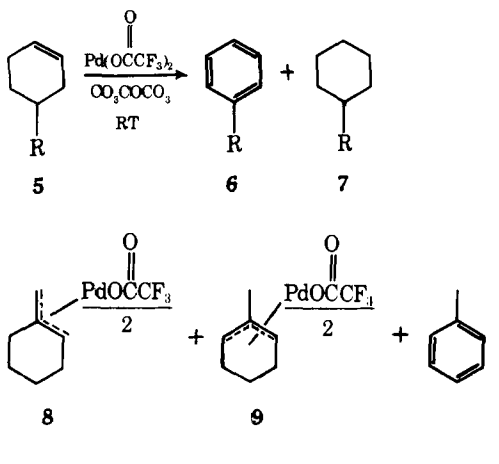
Indeed, this facile reaction is a general approach to acyclic π-allylpalladium complexes as summarized in Table I. The chemoselectivity is higher than those of previously described methods. For example, geranylacetone (entry 6) produced only the terminal complex in 54% yield or, based upon recovered starting material, in 83% yield. An almost 1:1 ratio was obtained under earlier conditions.[11] The selectivity presumably reflects the electronic deactivating influence of the carbonyl group on the 5,6 double bond. A similar chemoselectivity was observed in entry 9, although here the rather different degrees of steric hindrance account for the selectivity. Ketones (entries 2, 5, and 6) and esters (entries 4 and 9) are compatible. While most work was performed in acetone, ethyl acetate and THF (entries 3 and 4) are equally satisfactory. For terminal olefins, employing freshly dried solvents improves the yields. Stereochemistry of the starting olefin does not determine the stereochemistry of the π-allylpalladium complexes. In all cases only the syn complexes are observed. The easier obtention of pure products is illustrated by isolating the complex from geranylacetone as a crystalline solid, whereas previously[11] it was obtained only as an oil, although still analytically pure.

While acyclic olefins and olefins exocyclic to a polycyclic ring system behave normally, endocyclic olefins and simple methylenecycloalkanes behave quite differently. Treatment of cyclohexane in acetone-d_6 led in minutes at room temperature to benzene and cyclohexane. Similar results were obtained with 4-*tert*-butylcyclohexene. Both methylenecyclohexane and 1-methylcyclohexene produce mainly toluene, although signals corresponding to the complexes **8** and **9** were detected—especially in the early stages of the reaction. The

Table II. Catalytic Dehydrogenation of Cyclohexenes[a]

entry	olefin	solvent	time, h	product	yield,[b]	% conversion[c]
1		acetone	2		35	75
2		diglyme	17		95	60
3		diglyme	17		74	65

[a] All reactions employed 5 mol % palladium trifluoroacetate and 3 equiv of maleic acid at the reflux temperature of the indicated solvent. [b] Yields based upon recovered starting material. [c] Determined by NMR analysis.



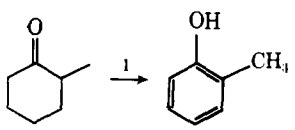
5 **6** **7**

8 **9**

disproportionation reaction is catalytic in **1**. Treatment of **5** (R = t-C_4H_9) with 5 mol % **1** led to a 40:60 mixture of **6** (R = t-C_4H_9) and **7** (R = t-C_4H_9) in 87% crude yield.

The disproportionation suggested the intermediacy of a palladium hydride species. Alternative acceptors were sought. 1-Hexene, methyl acrylate, and norbornadiene inhibit the reaction. Methyl crotonate and biacetyl do not inhibit reaction but also do not serve as palladium hydride acceptors. Maleic anhydride serves as a suitable palladium hydride acceptor but also inhibits the reaction to some degree. Dimethyl fumarate and maleic acid appear to be the acceptors of choice, with the latter preferred because of its ease of removal. Table II summarizes the results using 5 mol % palladium trifluoroacetate and 3 equiv of maleic acid. Although the conversion under these conditions did not exceed 75% even with prolonged reaction times, the conditions are reasonably mild.

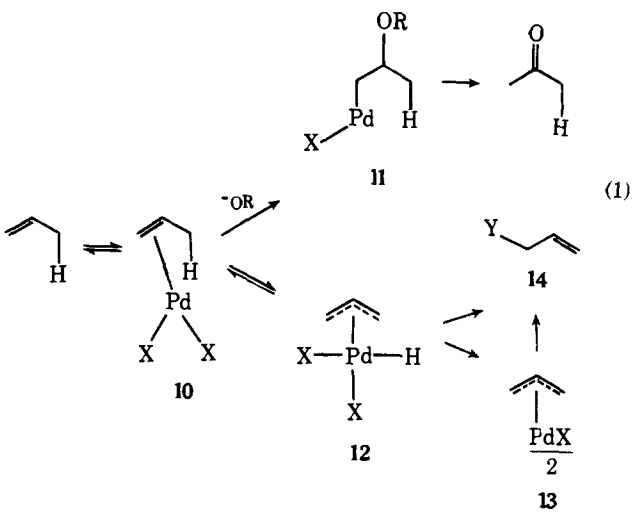
In an ancillary study, we examined the case of 2-methylcyclohexanone. Treatment with **1** produced 2-methylphenol in a rather slow reaction. The sluggishness of this reaction



accounts for the successful generation of the π-allyl complex from dihydrocarvone (Table I, entry 2).

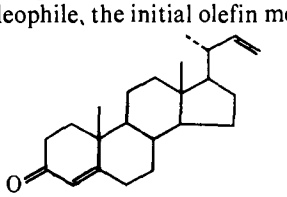
Discussion

A uniform picture begins to emerge for the reaction of olefins with palladium salts and is represented schematically in eq 1. The first step can be a preequilibrium or, in some instances, may become rate determining as indicated by the kinetic deactivation of alkyl substituents as well as by neighboring steric bulk; e.g., **15** was recovered unchanged. In the presence of a nucleophile, the initial olefin metal complex **10**



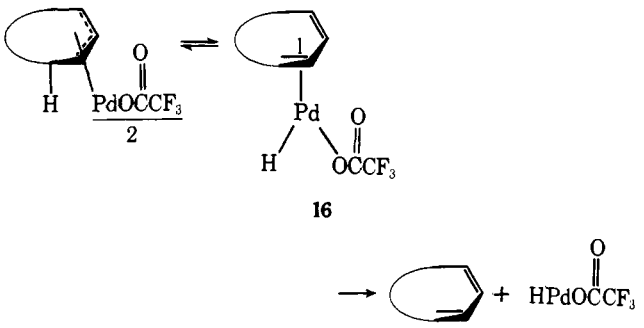
10 **11** **12** **13** **14**

(1)



15

undergoes nucleophilic attack to give **11**, which ultimately leads to oxidation product.[1,2,18] If the palladium is highly electrophilic, insertion into the allylic C–H bond can compete with nucleophilic attack to give **12**.[11c] Independent support for this insertion arises in the stereochemistry of formation of such complexes in which the hydrogen syn to the palladium is specifically removed.[22] Intermediate **12** can undergo loss of the elements of HX to give the π-allyl complex **13** or directly transfer a nucleophilic group, such as acetate, to give the product of allylic oxidation **14**. Under the previous conditions, high chloride ion concentration to ensure X = Cl and not X = OAc was necessary for good yields of π-allylpalladium complexes. Alternatively, the π-allyl complex **13** can be the source of the allylic oxidation product either by attack of an external nucleophile or internal delivery of X.[23] For the case of X = trifluoroacetate, this group is sufficiently nonnucleophilic that decomposition to **14** does not occur in contrast to the more nucleophilic acetate. If the complex can exist with no anti substituents, **13** (X = CF_3CO_2) is relatively stable. In the case of the cycloalkenes where the substituents are forced into the anti orientation, the close proximity of a hydrogen of the anti alkyl substituent to the electrophilic palladium can lead to insertion to produce **16**, which dissociates to the diene and



16

hydridopalladium trifluoroacetate. The latter can either transfer hydrogen or eliminate trifluoroacetic acid and generate a highly active and finely dispersed form of metallic palladium. Indeed, precipitation of a very fine powder is detected. This reactive metallic palladium appears to be responsible for the facile and catalytic nature of the disproportionation reaction.[24] Contrasting palladium trifluoroacetate with palladium acetate in such a reaction shows that the former effects complete conversion of cyclohexene to cyclohexane and benzene in less than 15 min at room temperature in acetone, whereas the latter requires more than 24 h under identical conditions. With palladium acetate, a suspension of palladium(0) is also noted. If the active disproportionation catalyst is the dispersed metallic palladium, the nature of this heterogeneous catalyst must be a function of the starting palladium salt. While the reactions of cyclopentene and cyclooctene were explored, they did not lead to characterizable products. Only in the case of cyclohexenes does this process lead to a clean reaction since the initial products can fall into the thermodynamic sink of an aromatic molecule. The absence of such a favorable hydrogen for insertion in the syn complexes accounts for their enhanced stability and the successful formation of π-allyl complexes as summarized in Table I.

The aromatization of methylenecyclohexane suggests that rapid isomerization of the initial complex to an endocyclic isomer occurs. Such an isomerization can proceed via conversion of the kinetically formed complex **8** to isomerized olefin, 1-methylcyclohexene, which then is converted to **9**. Indeed, 1-methylcyclohexene is detected in these reactions. Olefin isomerization arising from reversible formation of π-allyl complexes in the presence of HCl has been previously noted.[7] In the current cases, a similar isomerization could be effected by the trifluoroacetic acid produced in these reactions. Attempts to neutralize the acid in order to avoid such isomerizations with pyridine, 2,6-dimethylpyridine, or triethylamine led to complete inhibition of the total reaction.

The preparative advantages of this new method are immense. Two features stand out: (1) 1:1 stoichiometry of olefin and palladium salt and (2) successful use of monosubstituted olefins. For example, for incorporation of steroid side chains, where the olefin is as valuable as the metal, this new approach (Table I, entry 9) represents a major advance.[15d,25] The competing oxidation reactions of monosubstituted olefins are suppressed relative to the formation of π-allyl complexes—a fact which allows ready extension of allylic alkylation to monosubstituted olefins. The possibility that such a reaction can lead to a facile allylic oxidation and to a catalytic allylic alkylation forms a major avenue for our future work.

Most recently it has been noted that it is difficult to convert monosubstituted olefins directly to their π-allyl complexes.[27] This methodology overcomes that deficiency.

Experimental Section

General. All reactions were run under a positive nitrogen pressure. Acetone was dried over calcium sulfate, filtered, distilled, and kept over 4 Å molecular sieves. Reagent grade ethyl acetate was stored with 4 Å molecular sieves. THF was distilled over sodium benzophenone ketyl. ^{1}H NMR spectra were run on Jeolco MH-100 spectrometers. ^{13}C NMR spectra were taken on a Jeolco FX-60 spectrometer with wide-band ^{1}H decoupling. IR spectra were taken on a Perkin-Elmer 267 spectrometer. Mass spectra were obtained on an AEI-MS-902 spectrometer. Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Microanalyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, Mich.

Thin layer chromatography was performed with 20 × 20 cm plates, using Macherey-Nagel silica gel (P/UV 254). The solvent was a mixture of hexane and ethyl acetate. Compounds were removed by repeated washings with ethyl acetate. Column chromatography was performed on Grace silica gel, grade 62, mesh size 60-200 (Davidson Chemical).

Olefins (*Z*)-Geranylacetone was obtained from Professor W. G. Dauben. 2-Methyl-1-heptene was prepared by the standard Wittig olefination,[26] using methyltriphenylphosphonium bromide and 2-heptanone. 3-β-Hydroxyandrost-5-en-17-one was obtained from Roussel-Uclaf (France) and converted to 3-β-acetoxy-17-ethylidenandrost-5-ene by first treatment with triphenylphosphonium ethylide via a procedure previously described[15d] (83% yield) and then acetylation with acetyl chloride and pyridine in methylene chloride (90% yield). It can be recrystallized from ethanol, mp 80-84 °C. NMR ($CDCl_3$): δ 5.39 (d, J = 4.5 Hz, H-6), 5.13 (bq, J = 7 Hz, H-20), 4.61 (m, H-3), 2.6-1.0 (m, other H), 2.00 (s, acetyl), 1.00, 0.86 (2 s, Me-18 and Me-19); the presence of minor *E* isomer is suggested by the observation of a small singlet at 0.75 ppm (5-10%). IR (KBr): 1730 cm^{-1}. Calcd for $C_{22}H_{34}O_2$: 342.2558. Found: 342.2560. All other olefins were commercial samples.

Preparation of Palladium Bis(trifluoroacetate). From Pd(OAc)$_2$. The convenient procedure reported by Wilkinson et al.[17] was used, without further purification.

From PdCl$_2$. The procedure was inspired from a preparation of palladium acetate.[19] Palladium chloride (35.5 mg, 0.2 mmol) in 40 μL of 1 N aqueous HCl and 100 μL of water is heated with stirring up to 85 °C. Then 200 μL of 15% NaOH is added, and heating maintained for 5 min. The former homogeneous solution turns darker and a brown precipitate appears. A brown powder (41 mg of PdO·nH$_2$O) is collected by filtration on paper. It is dissolved in 250 μL of trifluoroacetic acid and stirred either for 2 h at room temperature or, better, for 5 min at 80 °C. Excess trifluoroacetic acid is removed in vacuo. The light brown powder (55 mg, 89%, at 80 °C) is collected and dried in vacuo (IR (KBr): 1690, 1435 cm^{-1}), and is identical with the material prepared by the preceding procedure.

Preparation of Bis[trifluoroaceto(7,1,2-*trihapto*pinene)palladium(II)]. β-Pinene (41 mg, 0.3 mmol) and palladium trifluoroacetate (93 mg, 0.3 mmol) in 2 mL of acetone were stirred at room temperature during 30 min. After concentration in vacuo, the oily residue was crystallized with hexane in the cold, yielding 66 mg (54%) of yellow-green crystals, mp 116-118 °C dec. ^{1}H NMR ($CDCl_3$): δ 4.00 (d, J = 5 Hz, H-2), 3.76 (s, anti H-7), 2.89 (s, syn H-7), 2.8-1.4 (m, other H), 1.37, 0.97 (2 s, 2 Me). ^{13}C NMR ($CDCl_3$): δ 165.29 (q, J_{CCF} = 41 Hz, C=O), 140.01 (s, C-2), 116.49 (q, J_{CF} = 293 Hz, CF_3), 68.62 (s, C-3), 53.28 (s, C-7), 45.99 (s, C-1), 39.58, 37.82, 35.22 (C-5, C-6, C-8), 29.76, 25.84, 21.75 (C-4, C-9, C-10). IR (KBR): 1690 cm^{-1} (broad). Anal. Calcd for $C_{24}H_{30}F_6O_4Pd_2$: C, 40.64; H, 4.27. Found: C, 40.70, H, 4.25.

General Procedure for Preparation of π-Allylpalladium Chloride Complexes. Preparation of Bis[chloro(9,10,11-*trihapto*methyl 10-undecenoate)palladium (II)]. Methyl 10-undecenoate (99 mg, 0.5 mmol) and palladium trifluoroacetate (154 mg, 0.5 mmol) in 4 mL of dried acetone were stirred at ambient temperature during 30 min. Tetra-*n*-butylammonium chloride (125 mg, 0.55 mmol) in 1 mL of dried acetone was added. The resulting mixture was stirred for 10 min. It was then filtered through Celite to remove any metallic palladium. The solvent and formed trifluoroacetic acid were removed in vacuo to yield an oil that was purified by TLC (one 20 × 20 cm plate; 1:1 hexane-ethyl acetate). Extraction of the yellow band (R_f 0.38-0.48) with ethyl acetate gave 110 mg (68%) of yellow crystals that could be recrystallized from hexane-chloroform, mp 86-87 °C. NMR ($CDCl_3$): δ 5.24 (td, J = 12, 7 Hz, H-10), 3.86 (d, J = 7 Hz, anti H-11), 3.8 (m, syn H-11), 3.60 (s, OMe), 2.81 (d, J = 12 Hz, H-9), 2.29 (t, J = 7 Hz, H-2), 1.3-1.8 (m, other CH_2). IR (KBr): 1735 cm^{-1}. Anal. Calcd for $C_{24}H_{42}Cl_2O_2Pd_2$: C, 44.60; H, 6.55; Cl, 10.97. Found: C, 44.31; H, 6.55; Cl, 11.05. Table III lists experimental details for all cases. The following data give the spectroscopic properties and microanalyses data.

Table III. Experimental Details

olefin (mg, mmol)	$Pd(OCOCF_3)_2$, mg, mmol	time	solvent	n-$Bu_4N^+Cl^-$, mg, mmol (10 min)	complex, mg, % yield	mp, °C	lit. mp, °C
(*E*)-5-decene (84, 0.6)	185, 0.6	30 min	acetone	150, 0.66	117, 70	128-129[a]	
5-isopropenyl-2-methylcyclohexanone (61, 0.4)	123, 0.4	~15 h	acetone	100, 0.44	77, 66	170-173[b] dec	
1-decene (56, 0.4)	123, 0.4	30 min	acetone	100, 0.44	77, 68	65-67[a]	
(42, 0.3)	93, 0.4	30 min	EtOAc	75, 0.33	54, 64	65-67	
(42, 0.3)	93, 0.3	30 min	THF	75, 0.33	42, 40	65-67	
methyl 10-undecenoate (99, 0.5)	154, 0.5	30 min	acetone	125, 0.55	110, 68	86-87[b]	
(59, 0.3)	93, 0.3	30 min	EtOAc	75, 0.33	76, 78	86-87	
(59, 0.3)	93, 0.3	30 min	THF	75, 0.33	80, 82	86-87	
6-methyl-5-hepten-2-one (101, 0.8)	247, 0.8	30 min	acetone	201, 0.88	150, 70	136.5-139.5[b] dec	
(*E*)-geranylactone (97, 0.5)	154, 0.5	30 min	acetone	125, 0.55	91,[c] 54	65-68[b]	oil
2-methyl-1-heptene (56, 0.5)	154, 0.5	3 h	acetone	125, 0.55	91, 80	53-54[a]	
β-pinene (68, 0.5)	154, 0.5	30 min	acetone	125, 0.55	116, 83	169-171[a] dec	161 168
3-β-acetyloxy-17-ethenylidenandrost-5-ene (104, 0.3)	93, 0.3	30 min	acetone	75, 0.33	133, 92	189-194[a] dec	

[a] Recrystallized from hexane. [b] Recrystallized from a mixture of hexane and chloroform. [c] Starting material is recovered with an isolated yield of 29%. Yield of complex based upon recovered starting material is 83%.

Bis[chloro(4,5,6-*trihapto*-5-decene)palladium(II)]. NMR (CCl_4): δ 5.19 (t, J = 11 Hz, H-5), 3.72 (m, H-4 and H-6), 1.6 (m, 4 CH_2), 0.9 (m, 2 Me). Anal. Calcd for $C_{20}H_{38}Cl_2Pd_2$: C, 42.73; H, 6.81; Cl, 12.61. Found: C, 42.68; H, 6.94; Cl, 12.37.

Bis[chloro(1′,2′,3′-*trihapto*-5-isopropenyl-2-methylcyclohexanone)palladium(II)]. NMR ($CDCl_3$): δ 3.84 (s, anti H-1′ and H-3′), 2.83 (s, syn H-1′ and H-3′), 1.0-2.9 (m, 8 ring H), 1.03 (d, J = 6 Hz, Me). IR (KBr): 1710 cm^{-1}. Anal. Calcd for $C_{20}H_{30}Cl_2O_2Pd_2$: C, 40.98; H, 5.16; Cl, 12.10. Found: C, 41.02; H, 5.03; Cl, 12.15.

Bis[chloro(1,2,3-*trihapto*-1-decene)palladium(II)]. NMR (CCl_4): δ 5.21 (td, J = 12.5, 7 Hz, H-2), 3.8 (m, H-3), 3.77 (d, J = 7 Hz, anti H-1), 2.74 (d, J = 12.5 Hz, syn H-1), 1.6 (m, CH_2-4), 1.3 (m, CH_2-5 to 9), 0.88 (m, Me). Anal. Calcd for $C_{20}H_{38}Cl_2Pd_2$: C, 42.73; H, 6.81; Cl, 12.61. Found: C, 42.75; H, 6.84; Cl, 12.62.

Bis[chloro(5,6,7-*trihapto*-6-methyl-5-hepten-2-one)palladium(II)]. NMR ($CDCl_3$): δ 3.70 (s, anti H-1), 3.46 (t, J = 6.5 Hz, syn H-1), 2.78 (m, CH_2-3), 2.65 (s, syn H-1), 2.15, 2.10 (2 s, 2 Me), 1.79 (m, CH_2-4). IR (KBr): 1710 cm^{-1}. Anal. Calcd for $C_{16}H_{26}Cl_2O_2Pd_2$: C, 35.98; H, 4.91; Cl, 13.28. Found: C, 36.05; H, 4.78; Cl, 13.23.

Bis[chloro(9,10,11-*trihapto*-(*E*)-6,10-dimethyl-5,9-undecadien-2-one)palladium(II)]. NMR: identical with the one reported[11] in the literature. IR (KBr): 1710 cm^{-1}.

Mixture of Bis[chloro(1,2,β-*trihapto*-2-methyl-1-heptene)palladium(II)] (A) and Bis[chloro(1,2,3-*trihapto*-2-methyl-1-heptene)palladium(II)] (B). NMR ($CDCl_3$): δ 3.91 (s, syn H-1 and H-β of A), 3.71 (s, syn H-1 of B), 3.6 (m, H-3 of B), 2.84 (s, anti H-1 and H-β of A), 2.67 (s, anti H-1 of B), 2.31 (t, J = 7 Hz, CH_2-3 of A), 2.06 (s, Me-2 of B), 1.8-1.2 (m, other CH_2), 0.89 (m, Me-7 of A and B). Anal. Calcd for $C_{16}H_{30}Cl_2Pd_2$: C, 37.97; H, 5.97; Cl, 14.01. Found: C, 37.95; H, 5.94; Cl, 13.95.

Bis[chloro(7,1,2-*trihapto*pinene)palladium(II)]. NMR ($CDCl_3$): identical with the one reported[11] in the literature.

Bis[chloro(16,17,β-*trihapto*-3-β-acetyloxy-17-ethenylidenandrost-5-ene)palladium(II)]. NMR ($CDCl_3$): δ 5.37 (d, J = 4.2 Hz, H-6), 4.61 (m, H-3), 3.72 (m, H-16 and H-20), 2.4-1.0 (m, other H), 2.04 (s, COMe), 1.29 (d, J = 6.6 Hz, Me-21), 1.05, 1.02 (2 s, Me-18 and Me-19); the presence of the minor anti isomer could not be ascertained. IR (KBr): 1730 cm^{-1}. Anal. Calcd for $C_{46}H_{66}Cl_2O_4Pd_2$: C, 57.15; H, 6.88; Cl, 7.34. Found: C, 57.12; H, 6.97; Cl, 7.27.

Dehydrogenation Reactions. Of Methyl 3-Cyclohexene-1-carboxylate. A solution of 1.40 g (10 mmol) of methyl 3-cyclohexene-1-carboxylate, 154 mg (0.5 mmol) of palladium trifluoroacetate, and 3.48 g (30 mmol) of maleic acid in 25 mL of freshly distilled and dried diglyme was degassed and then refluxed for 17 h. It was poured into water and extracted with 2 × 50 mL of pentane. The pentane extracts were washed with 2 × 100 mL of aqueous sodium bicarbonate and then brine. After evaporation of the pentane through a Vigreux column, the residue was distilled in a Kugelrohr apparatus at 110-120 °C (15 mm) to give 1.151 g (85% yield) which by NMR spectroscopy consisted of 65% methyl benzoate with the remainder starting material.

Of Δ′-*p*-Methene. As above, 276 mg (2 mmol) of Δ′-*p*-menthene, 31 mg (0.1 mmol) of palladium trifluoroacetate, and 696 mg (6 mmol) of maleic acid in 5 mL of diglyme gave 266 mg (99% yield) of product consisting of 60% *p*-cymene and 40% *p*-menthene by NMR analysis.

Of 4-*tert*-Butylcyclohexene. A solution of 207 mg (1.5 mmol) of 4-*tert*-butylcyclohexene, 23 mg (0.075 mmol) of palladium trifluoroacetate, and 522 mg (4.5 mmol) of maleic acid in 5 mL of dry acetone gave, after 2 h at reflux, workup as above, and Kugelrohr distillation at 80 °C (105 mm), 86.4 mg (43%) which by NMR was 75% *tert*-butylbenzene and 25% 4-*tert*-butylcyclohexene.

Acknowledgment. We wish to thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of our programs. We express special thanks to Professor W. G. Dauben for a gift of (*E*-geranylacetone and Roussel-Uclaf for 3-β-hydroxyandrost-5-en-17-one. We thank Englehardt Industries for a generous gift of palladium chloride.

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Metalation of 1,3-Dithiolanes. Mercaptan Synthesis and Carbonyl Transposition

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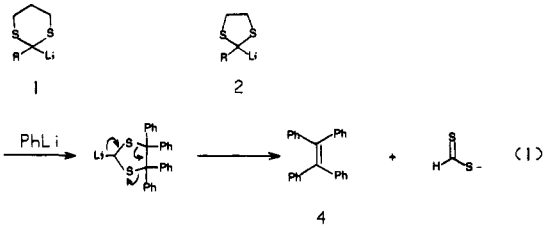
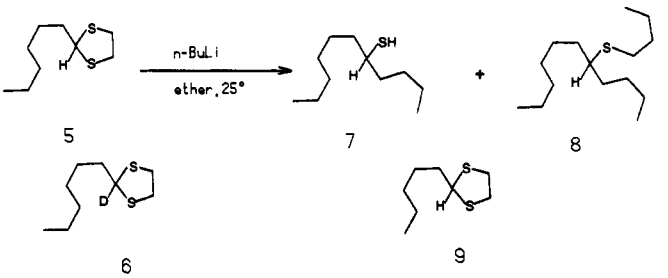
Abstract: The reaction of 1,3-dithiolanes with *n*-butyllithium results in fragmentation to the corresponding thiocarbonyl compound followed by further reaction with *n*-butyllithium. All four types of thiocarbonyl reactions are observed: reduction, S-addition, C-addition, double addition. Synthetic applications of this reaction for the synthesis of secondary mercaptans and 1,2-carbonyl transposition (**23** → **24a–c**) are described.

Umpolung[1] of carbonyl reactivity via 1,3-dithiane anions such as **1** has had substantial impact on synthetic organic chemistry. In contrast, anion **2** has been reported[2,3] to undergo facile elimination to form ethylene. This hypothesis was apparently based on the work of Schönberg[4] (eq 1), who showed



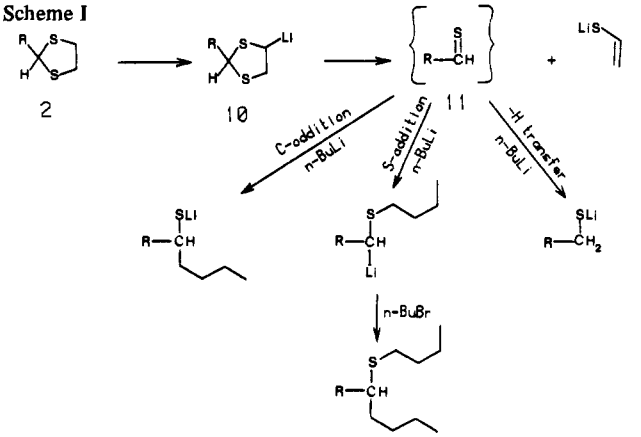
(1)

that compound **3** was cleaved with phenyllithium to tetraphenylethylene (**4**). Our results indicate that *the fragmentation shown in eq 1 is not the major mode of 1,3-dithiolane/n-butyllithium reaction.* When **5** was treated with 1 equiv of *n*-butyllithium in ether at −20 °C followed by D_2O (conditions under which the corresponding 1,3-dithiane is deuterated), no **6** could be detected by GC/MS. Excess (4 molar equiv) *n*-butyllithium in ether at 25 °C reacted with **5** to yield a product mixture (bp ~120 °C at 0.3 Torr, 91% yield) consisting of 73% **7** and 19% **8**. Thus 2-lithio-1,3-dithiolane is not formed under these conditions. The results of a number of reactions of **5** and **9** are summarized in Table I. There appears to be a solvent dependence, since **5** does not lead to significant cleavage in THF at 0 °C, conditions under which 2-lithio-1,3-dithiolane has been reported[6,7] to be stable.



Our mechanistic rationale[9] for the cleavage process is shown in Scheme I. All products obtained from this and subsequent

Scheme I



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