structure for N,N,N′,N′-tetramethylbenzidine mononitrate salt. **Anal.** Calcd for $C_{16}H_{21}N_3O_3$: C, 62.08; H, 7.22; N, 14.32. Found: C, 61.81; H, 6.83; N, 14.00.

The solution was not examined for further products.

Acknowledgments. The authors wish to thank Professor B. E. Conway and Dr. A. K. Hoffmann for valuable discussion.

Organic Syntheses by Means of Noble Metal Compounds. XXXIV.[1] Carbonylation and Decarbonylation Reactions Catalyzed by Palladium

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Abstract: The palladium-catalyzed decarbonylation of acyl halides and aldehydes to form olefins has been studied. The carbonylation of olefinic compounds and the decarbonylation of acyl halides and aldehydes as well as the Rosenmund reduction are discussed from a common mechanistic standpoint.

Recently the usefulness of palladium in organic syntheses has attracted much attention. The well-known Wacker process to form carbonyl compounds from olefins is a typical example.[2] In addition, we have shown that palladium is a versatile catalyst for the carbonylation of various compounds. For example, an olefin–palladium chloride complex is carbonylated at room temperature to form β-chloroacyl chloride with the reduction of divalent to zero-valent palladium.[3] Furthermore, metallic palladium catalyzes the carbonylation reaction of olefins to form saturated esters[4] and aldehydes,[5] and a brief mechanistic discussion has been given.[6,7] Also diolefins,[8–10] allylic compounds,[11,12] and acetylenic compounds[13–15] are carbonylated. Based on the mechanism of the carbonylation and an assumption that the carbonylation reaction is reversible, we expected that decarbonylation of aldehydes and acyl halides should be catalyzed by metallic palladium. We now have established that the decarbonylation of aldehydes and acyl halides can be carried out in the presence of a catalytic amount of metallic palladium and the scope of the reaction is described in this paper.

The formation of a true palladium carbonyl comparable to nickel carbonyl has not been reported and only carbonyl derivatives of palladium are known.[16,17] The metallic palladium catalyzed carbonylations proceed in the presence of some kind of hydrogen source. Hydrogen halides and molecular hydrogen are found to be satisfactory analogous to the nickel carbonyl catalyzed reaction, in which addition of hydrogen halide to form a hydrogen–nickel bond is assumed as prerequisite of the catalysis.[18] The question as to how the solid catalyst like metallic palladium can catalyze both carbonylation, which is usually possible only by complex transition metal carbonyl catalysts under homogeneous conditions, and decarbonylation is considered in this paper.

Results

Decarbonylation of Acyl Halides. In the presence of a catalytic amount of metallic palladium, it was found that acyl halides can be decarbonylated smoothly to give olefins, carbon monoxide, and hydrogen halides. The decarbonylation reaction of acyl halides to form olefins is a new reaction, and it is useful in organic syntheses to degrade acid derivatives by one carbon.

Higher aliphatic acyl chlorides and bromides were decarbonylated in high yields to give olefins having one less carbon atoms when they were heated with a catalytic amount of metallic palladium at 200°. Palladium black or palladium on carbon prepared for hydrogenation is satisfactory as the catalyst. The olefins produced were a mixture of isomeric inner olefins even when the olefins were distilled off from the reaction medium as soon as they were formed. The decarbonylation of acyl halides which have no β hydrogen gave alkyl halides with one less carbon atom. For

$$RCH_2CH_2COX \longrightarrow RCH{=}CH_2 + CO + HX$$

$$RCOX \longrightarrow RX + CO$$

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Table I. Decarbonylation of Acyl Halides Catalyzed by Metallic Palladium[a]

Acyl halide	Amt, g	Reaction Temp, °C	 Time, hr	Gas evolution (HCl + CO), ml	Product, %
$CH_3(CH_2)_8COCl$	20	200–230	10	2960	Nonene, 58
$CH_3(CH_2)_7COCl$	20	200–220	8	3000	Octene, 47
$CH_3(CH_2)_6COBr$	20	200–210	5	1762	Heptene, 66
$CH_3(CH_2)_{14}COCl$	16	200–220	8	1660	Pentadecene, 30
$C_6H_5CH_2CH_2COCl$	20	200–205	6	. . .	Styrene, 58
$C_6H_5CH_2COCl$	20	200–218	3	2283	Benzyl chloride, 42
C_6H_5COCl	10	200–210	24	100	Chlorobenzene, 5

[a] Well-dried Pd/C (5%), 1–2 g was used.

Table II. Decarbonylation of Acyl Halides Catalyzed by Noble Metal Compounds

Acid halide	Amt, g	Catalyst	Amt, g	Reaction Time, hr	 Temp, °C	Gas evolution (CO + HCl), ml	Product, %	Yield
$CH_3(CH_2)_8COCl$	5	$PdCl_2$	0.1	1.5	200	1050	Nonene	90.2
$CH_3(CH_2)_7COCl$	5	$PdCl_2$	0.2	1.5	200	855	Octene	83
$CH_3(CH_2)_6COBr$	5	$PdCl_2$	0.2	1.5	200	750	*trans*-2- and 3-heptene (76) *cis*-2- and 3-heptene } (24) 1-heptene }	80
$CH_3(CH_2)_5COBr$	5	$PdCl_2$	0.1	1.0	200		1-Hexene (7.5), 2- and 3-hexene (92.5)	80
$C_6H_5CH_2CH_2COCl$	10	$PdCl_2$	0.2	1.0	200	1780	Styrene	53
CH_2CH_2COCl | CH_2CH_2COCl	8	$PdCl_2$	0.2	0.5	180	545	Cyclopentanone	30
$CH_2(CH_2)_8COCl$	5	Pd(acetylacetone)$_2$	0.2	1.5	200	. . .	Nonene	80
$CH_3(CH_2)_8COCl$	5	$PdCl_2(C_6H_5CN)_2$	0.2	1.5	200	240	Nonene	20
$CH_3(CH_2)_8COCl$	5	PdO	0.2	2.0	200	. . .	Nonene	86
$CH_3(CH_2)_8COCl$	5	$Pd(NO_3)_2$	0.2	1.5	200	850	Nonene	76
$CH_3(CH_2)_8COCl$	5	$RhCl_3$	0.2	1.5	200		Nonene	86
$CH_3(CH_2)_8COCl$	5	Rh	0.1	0.3	200	915	Nonene	85
c-$C_8H_{15}COCl$	5	$PdCl_2$	0.2	3	260	715	Cyclooctene	41
C_6H_5COCl	5	Rh	0.2	3	200	20	Chlorobenzene	Trace

example, decanoyl chloride was converted into a mixture of isomeric nonenes in a good yield. In addition, a small amount of dinonyl ketone was obtained from the residue in a flask. Hexenes obtained by the decarbonylation of heptanoyl bromide consisted of 7.5% of 1-hexene and 92.5% of a mixture of 2- and 3-hexenes.

When the double bond migration of olefins produced by the decarbonylation was impossible, some other products were formed in addition to olefins. When phenylpropionyl chloride was decarbonylated, the main products were styrene (53%) and 1,5-diphenyl-1-penten-3-one (10%) with a small amount of unidentified products.

$$C_6H_5CH_2CH_2COCl \longrightarrow C_6H_5CH{=}CH_2 + C_6H_5CH_2CH_2COCH{=}CHC_6H_5 + \text{others}$$

Phenylacetyl chloride was decarbonylated to give benzyl chloride, but in this case also an unidentified product which has a higher molecular weight was formed in a considerable amount. In contrast to the aliphatic acyl halides which gave olefins in good yields, aromatic acid halides were not decarbonylated satisfactorily. The results of the decarbonylation using metallic palladium as the catalyst are shown in Table I.

The catalytic activities of other noble metal salts and oxides were investigated. It was found that palladium chloride, palladium nitrate, palladium oxide, palladium acetylacetonate, rhodium trichloride, and rhodium oxide were active catalysts of the decarbonylation. On the other hand, platinum on charcoal, platinum chloride, rhenium trichloride and pentachloride, ruthenium trichloride, and iridium trichloride were found to be inactive. The results of the decarbonylation using these catalysts are shown in Table II. The palladium salts were easily reduced to black metallic palladium when they were heated to 150° in acyl chlorides and since the catalytic activity of the palladium salts, especially palladium chloride, was much higher than that of metallic palladium, it is advisable to use a catalytic amount of palladium chloride, rather than metallic palladium, for more efficient decarbonylation (*cf.* Tables I and II).

Decarbonylation of Aldehydes. The decarbonylation of some aldehydes catalyzed by metallic palladium has been known for some time.[19–25] This reaction was reinvestigated. It seems likely that the decarbonylation can be applied to any aldehydes if the temperature is at least 200°. Therefore, aldehydes which have boiling points higher than 200° can be decarbonylated easily by heating with a catalytic amount of palladium. Although no exact studies have been carried out, lower boiling aldehydes can be

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Table III. Decarbonylation of Aldehydes

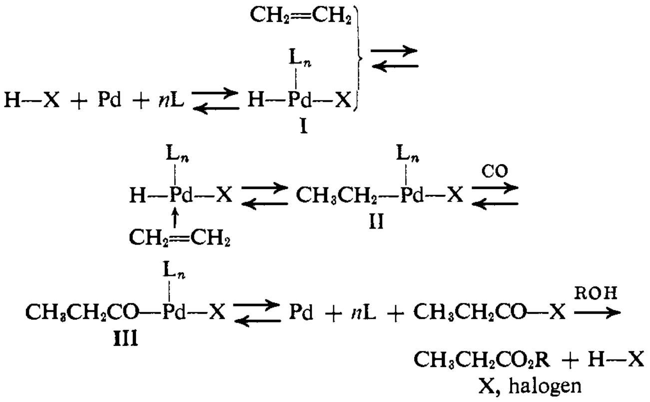
Aldehyde	Amt, g	Pd-C (5%), g	Reaction Time, °C	Reaction Time, min	Product, % Olefin	Product, % Paraffin	Gas evolution, ml H_2	Gas evolution, ml CO
$CH_3(CH_2)_8CHO$	2.82	0.15	190 ± 5	135	Nonene, 57	Nonane, 27	342	378 (93%)
$C_6H_5CH_2CH_2CHO$	5.1	0.49	185 ± 5	120	Styrene, trace	Ethylbenzene, 37	Trace	472 (55%)

decarbonylated in the gas phase by supported palladium catalyst at 200°. Some results are shown in Table III. Products of the decarbonylation of aldehydes are a mixture of olefins and paraffins, the ratio depending on the reaction conditions and aldehydes. For example, by the decarbonylation of β-phenylpropionaldehyde, ethylbenzene was obtained as a sole product and the amount of styrene was negligible. Furthermore, when decanal was decarbonylated both nonene and nonane were formed and the volume of hydrogen evolved was larger than that corresponding to nonene produced. Therefore, dehydrogenation reaction to give unidentified products must have occurred.

Discussion

Mechanism of the Carbonylation and Decarbonylation. Based on the experimental results of carbonylation and decarbonylation reactions, the mechanism given in Scheme I is proposed for both reactions.

Scheme I



$$\text{H—X} + \text{Pd} + n\text{L} \rightleftarrows \underset{\text{I}}{\overset{\text{L}_n}{\text{H—Pd—X}}} \rightleftarrows \overset{\text{L}_n}{\text{H—Pd—X}} \leftarrow \text{CH}_2{=}\text{CH}_2$$

$$\overset{\text{L}_n}{\text{H—Pd—X}} \rightleftarrows \underset{\text{II}}{\text{CH}_3\text{CH}_2\text{—}\overset{\text{L}_n}{\text{Pd}}\text{—X}} \overset{\text{CO}}{\rightleftarrows}$$

$$\underset{\text{III}}{\text{CH}_3\text{CH}_2\text{CO—}\overset{\text{L}_n}{\text{Pd}}\text{—X}} \rightleftarrows \text{Pd} + n\text{L} + \text{CH}_3\text{CH}_2\text{CO—X} \xrightarrow{\text{ROH}} \text{CH}_3\text{CH}_2\text{CO}_2\text{R} + \text{H—X}$$

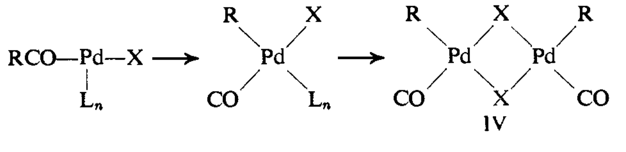
X, halogen

The first step of the metal palladium catalyzed carbonylation of simple olefins in the presence of hydrogen halide seems to be the formation of Pd(II) species which is expressed for convenience as $H\text{-}Pd\text{-}X(L)_n$ (I) by the oxidative addition of hydrogen halides to metallic palladium in the presence of suitable ligands L. L, used in this mechanism, is a ligand which can stabilize palladium and satisfy a coordination number of the palladium whatever it is. L can be carbon monoxide and sometimes solvent or another molecule of palladium. The next step is the insertion of the olefin into the H-Pd bond to form the alkyl complex (II), followed by conversion to an acyl complex (III) by carbon monoxide insertion.[26] Finally the acyl complex collapses to form acyl halide and zero-valent palladium. The acyl halide is converted into an ester and hydrogen halide in alcohol. The regeneration of metallic palladium and hydrogen halide makes the whole carbonylation reaction catalytic. An important point in this mechanism is the postulated formation of the species H-Pd-X (I). Some solution of palladium apparently does occur because after the carbonylation reaction, when precipitated palladium is removed by filtration, the work-up of the clean filtrate produces additional metallic palladium. Formation of a hydride complex by oxidative addition of hydrogen halides or hydrogen to transition metal complexes is well known[27,28] and the metal hydride complexes thus formed play an important role in the metal complex catalyzed reactions such as homogeneous hydrogenation, carbonylation, double bond isomerization, and addition reactions. A similar reaction might be possible with palladium under the carbonylation conditions. The mechanism of the formation of aldehydes can be explained by replacing X in Scheme I with H, except for the last step of the esterification.

It is well known that some steps of metal carbonyl catalyzed carbonylation reactions are reversible. For example, the reversible conversion of *trans*-(acetyl)-triphenylphosphinemanganese tetracarbonyl to *cis*-(methyl)triphenylphosphinemanganese tetracarbonyl[29,30] and reversible carbonylation of platinum and palladium phosphine complexes have been reported.[31]

The first step of the decarbonylation is assumed to be the oxidative addition of acyl halides or aldehydes to metallic palladium to form the acyl–palladium complex (III) in accordance with established analogous reactions.[32–34] On the other hand, the formation of the acyl complex (III, X = H) by the addition of aldehyde is not a known reaction. It seems possible that both acyl halides and aldehydes form acyl–palladium complexes when they are contacted with metallic palladium at fairly high temperature by the oxidative addition. Although there is no direct evidence of the complex formation, it was observed that metallic palladium partially dissolved in acyl halides.

The transformation of the acyl–palladium complexes to the alkyl–palladium complexes (II) in the absence of carbon monoxide at high temperature is reasonable.[34] This transformation would be facilitated by a possibility that a rather stable 4-coordinate halogen bridged carbonyl complex (IV) is formed. Finally, the alkyl–palladium bonds are split to afford olefins and hydrogen halide, or hydrogen. It is known that alkyl palladium



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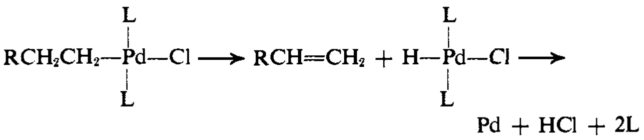
phosphine complexes with β-hydrogen atoms in the alkyl group are unstable and decompose by β-hydrogen elimination to give an olefin and palladium hydride.[35] The latter then decomposes to give zero-valent palladium and hydrogen halide. Moiseev and Vargaftik



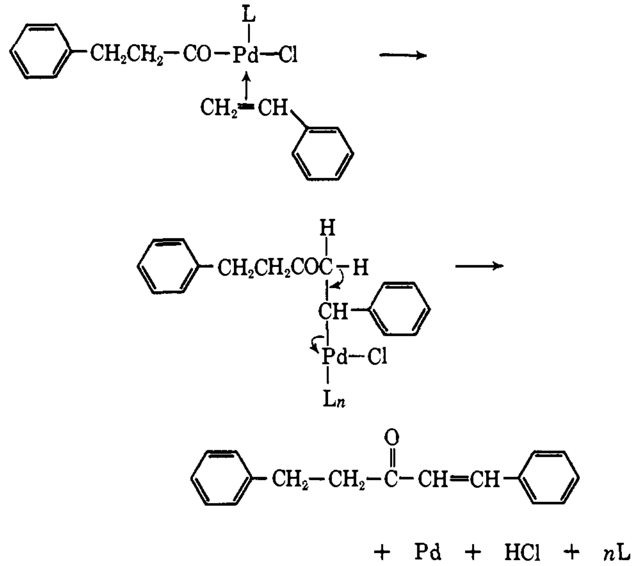
$$\mathrm{RCH_2CH_2{-}\overset{L}{\underset{L}{Pd}}{-}Cl \longrightarrow RCH{=}CH_2 + H{-}\overset{L}{\underset{L}{Pd}}{-}Cl \longrightarrow Pd + HCl + 2L}$$

L, phosphine

studied the decomposition of the alkyl–palladium bond by the reaction of ethylmagnesium bromide with palladium chloride in ether.[36] Equal amounts of ethylene and ethane were formed by the reactions

$$C_2H_5MgBr + PdCl_2 \longrightarrow C_2H_5PdCl + MgBrCl$$
$$C_2H_5PdCl \longrightarrow CH_2{=}CH_2 + HCl + Pd$$
$$C_2H_5MgBr + HCl \longrightarrow CH_3CH_3 + MgBrCl$$

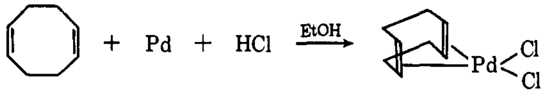
We have observed the formation of 1,5-diphenyl-1-penten-3-one by the decarbonylation of β-phenylpropionyl chloride. The formation of the ketone can be explained by the following scheme. The styrene formed by the decarbonylation coordinates with the intermediate acyl complex and then 3-ketoalkyl complex is formed by the olefin insertion. Finally β-hydrogen elimination gives the α,β-unsaturated ketone.



The isolation of the intermediate complexes postulated in Scheme I was attempted under various conditions but all failed. For example, an attempt to isolate the acyl complex by the reaction of acyl halides with metallic palladium was carried out in the presence of an excess of triphenylphosphine, which might stabilize the acyl complex as soon as it is formed. However, dichlorobis(triphenylphosphine)palladium was formed instead

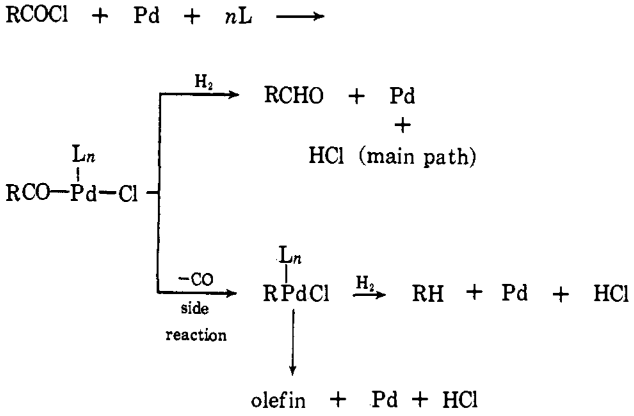
$$Pd + PPh_3 + RCOCl \longrightarrow (PPh_3)_2PdCl_2$$

of the acyl phosphine complex. A facile oxidation of palladium was also observed on treating metallic palladium with hydrogen halide and 1,5-cyclooctadiene in ethanol, whereupon the 1,5-cyclooctadiene–palladium chloride complex is formed.[8] Formation of π-allyl complex by the reaction of allyl bromide and metallic palladium is another example.[37] Oxidation reactions of zero-valent platinum and palladium phosphine complexes with hydrogen halides have been reported.[38] The mechanism of these oxidation reactions of palladium is not completely clear, but zero-valent palladium can be oxidized very easily in the presence of some suitable stabilizing ligands such as phosphines, carbon monoxide, or halogens.

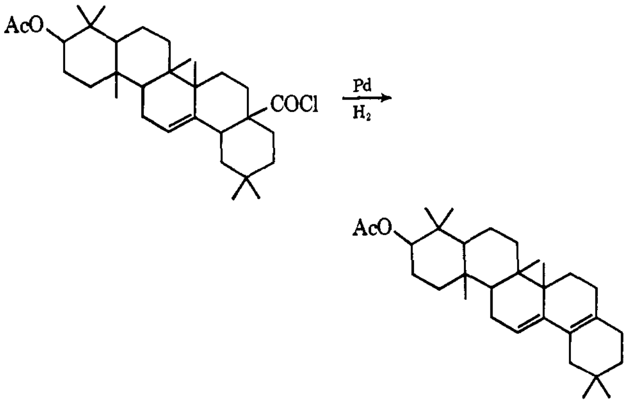


The mechanism of the well-known Rosenmund reduction is suggested from the experimental results and the mechanism of the carbonylation and decarbonylation.[6,39] The first step of the reduction seems to be the formation of an acyl–palladium bond by the oxidative addition of acyl halides to metallic palladium at about 100°, and it then reacts with hydrogen to form aldehydes and metallic palladium (Scheme II).

Scheme II



It is known that in the Rosenmund reduction some decarbonylated products are formed as by-products.[40,41] This side reaction can be explained by the "acyl–alkyl rearrangement," followed by hydrogenolysis. Olefin formation by an attempted Rosenmund reduction of the chloride of acetyloleanolic acid shown below was reported,[42] and the reaction can be explained by the mechanism shown in Scheme II. This example shows that even a sterically hindered angular group can be



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removed easily by palladium and suggests interesting synthetic usefulness.

Experimental Section

Materials. Commercially available palladium chloride, palladium nitrate, palladium oxide, metallic palladium, and rhodium trichloride trihydrate were used without further purification. Palladium on carbon was dried at 100° under reduced pressure before use. Acyl halides were prepared by the chlorination with thionyl chloride or by the bromination with phosphorus tribromide of the corresponding acids. The acyl halides were distilled before use. Most of the aldehydes were commercial products. β-Phenylpropionaldehyde was synthesized by the Rosenmund reduction of the corresponding acyl chloride.

Decarbonylation of Acyl Halides. General Procedure. In a 25–50-ml Claisen distilling flask, 8–20 g of freshly distilled acyl halides was placed and nitrogen was passed through the apparatus. The flask was heated to 200° or higher in an oil bath. Soon the evolution of hydrogen halide and carbon monoxide was observed and after a while, low-boiling olefin began to distil off. Reaction time and volume of the gas evolved are shown in the table. The structure of the collected olefins was determined by infrared and nmr spectra, molecular weight determination by mass spectroscopy, and gas chromatography. Positions of double bonds were determined by ozonolysis, followed by gas chromatography of the aldehydes formed. A typical example is as follows.

Decarbonylation of Decanoyl Chloride. In a 50-ml Claisen flask, 20 g of freshly distilled decanoyl chloride and 1 g of well-dried 1% palladium on carbon were placed. The end of the Claisen flask was connected with a gas buret filled with paraffin oil. The apparatus was swept with dry nitrogen. Then the flask was heated to 200° in an oil bath. Soon the evolution of gas consisting of carbon monoxide and hydrogen chloride was observed. When the evolution of the gas amounted to 200 ml, a low-boiling product began to distil. After about 10 hr, 7.9 g of the low-boiling product was collected. The product was redistilled. Infrared spectrum showed peaks at 3020, 2960, 2930, 2860, 2650, 1465, 1384, 965, and 910 cm^{-1}. Mass spectrum showed the molecular weight to be 126 (calcd for C_9H_{18}, 126). *Anal.* Calcd for C_9H_{18}: C, 85.70; H, 14.30. Found: C, 85.50; H, 14.41. These data support that the product was nonene. When hydrogenated in the presence of palladium on carbon, the nonene mixture absorbed 1 equiv of hydrogen. Gas chromatography showed one peak. The molecular weight determined by mass spectrum was 128 (calcd for C_9H_{20}, 128). Nmr and infrared spectra were identical with those of an authentic sample of nonane. *Anal.* Calcd for C_9H_{20}: C, 84.28; H, 15.72. Found: C, 84.18; H, 15.67. The ozonization of the mixed nonenes, followed by hydrogenation, gave C_1–C_8 straight-chain aldehydes, which were identified by gas chromatographic analysis. The results show that the product consisted of 1-, 2-, 3-, and 4-nonenes.

The residue in the flask was washed with 20 ml of benzene, and the solution was filtered to remove palladium on carbon. The benzene layer was washed twice with 10 ml of 10% aqueous sodium carbonate solution, twice with water, and dried with anhydrous sodium sulfate. Evaporation of the solvent afforded 0.5 g of white crystal, which was recrystallized from ethanol. This product was identified as dinonyl ketone by the following evidences: infrared band, 1705 cm^{-1}; mp 58° (lit.[43] mp 58°). *Anal.* Calcd for $C_{19}H_{38}O$: C, 80.80; H, 13.50; mol wt, 282. Found: C, 80.61; H, 13.62; mol wt, 275 (by a Mechrolab vapor pressure osmometer).

Decarbonylation of β-Phenylpropionyl Chloride. In a 50-ml Claisen flask, 10 g of freshly distilled β-phenylpropionyl chloride and 0.2 g of palladium chloride were placed. The end of the Claisen distilling flask was connected with the gas buret filled with paraffin oil. The apparatus was swept with dry nitrogen. The flask was heated in an oil bath at 200°. Soon evolution of hydrogen chloride and carbon monoxide was observed. After 1 hr, the gas evolution amounted to 1780 ml and a low-boiling material distilled off. The low-boiling material was shown to be homogeneous by gas chromatography and was identified as styrene (yield, 3.2 g, 53%). The residue in the flask was washed with 50 ml of ether and separated from palladium metal by filtration. The ethereal layer was washed with water and dried. After evaporation of ether, residue was distilled and separated into two fractions. The lower boiling fraction, 1.3 g, bp 130° (0.8 mm), solidified on standing, which had mp 47–48° (lit.[44] 48.5°). Infrared spectrum was identical with that of β-phenylpropionic acid. The higher boiling fraction, 2 g, 170–210° (0.8 mm), was converted into the corresponding 2,4-dinitrophenylhydrazone, which was a mixture of yellow and red crystals. Fractional crystallization from ethyl acetate–hexane mixture gave 1.2 g of pure red crystals, which were identified as the dinitrophenylhydrazone of 1,5-diphenyl-1-penten-3-one, which had mp 162° (lit.[45] 162°). *Anal.* Calcd for $C_{23}H_{20}N_4O_4$: C, 66.3; H, 4.81; N, 13.46. Found: C, 66.37; H, 4.88; N, 13.37. The yellow crystals were not characterized.

Decarbonylation of Decanal. A mixture of 2.82 g of freshly distilled decanal and 0.15 g of well-dried palladium on carbon (5%) was placed in a 25-ml Claisen distilling flask, which was connected with the gas buret. The flask was heated between 190 and 195°. Evolution of gas was observed soon and a liquid distilled off. After 135 min, the evolution of the gas stopped and 1.92 g of the distillate and 720 ml of the gas were collected. The liquid was found to be a mixture of four components by gas chromatography (PEG 6000 + silver nitrate (30%), at 100° helium). One of the peaks was identified as nonane, and the other three peaks were found to be isomeric nonenes. The ratio of nonane to the nonene mixture was found to be 1:1. The gas collected was analyzed by gas chromatography (column, Molecular Sieve 5A, 2.5 *m*, nitrogen at 71°) and found to be a mixture of 378 ml of carbon monoxide and 342 ml of hydrogen.

Reaction of Benzoyl Chloride with Metallic Palladium in the Presence of Triphenylphosphine. In a 50-ml Claisen flask, 0.2 g of metallic palladium, 5 g of benzoyl chloride, 5 g of triphenylphosphine, and 20 ml of *p*-xylene were placed. The system was swept with argon and the mixture was heated to reflux. After 7 hr, yellow solid, which had deposited on the bottom of the flask, was collected by filtration. The solid was extracted with chloroform and yellow crystals were precipitated by the addition of *n*-hexane (yield, 0.68 g). The crystals were identified with an authentic sample of dichlorobis(triphenylphosphine)palladium by infrared spectrum and analysis. *Anal.* Calcd for $C_{36}H_{30}Cl_2P_6Pd$: C, 61.60; H, 4.28; Cl, 10.12; P, 8.83. Found: C, 61.58; H, 4.31; Cl, 10.70; P, 8.90.

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