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Palladium-Catalyzed Decarbonylation of Acyl Cyanides

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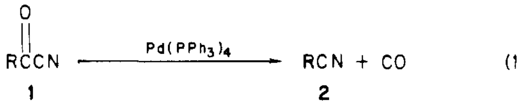
The palladium-catalyzed decarbonylation of aromatic and heteroaromatic acyl cyanides **1** gives the corresponding nitriles **2** in excellent yields. Alkylacyl cyanides can be converted into the corresponding alkenes via decarbonylation followed by β-elimination of hydrogen cyanide. Because of easy preparation of acyl cyanides by the oxidation of cyanohydrins, the present decarbonylation reaction provides an efficient method for the preparation of nitriles from aldehydes under mild and neutral conditions. The catalytic decarbonylation involves the following processes; oxidative addition of acyl cyanides **1** to $Pd(PPh_3)_4$ to give acylpalladium complexes **13**, acyl–aryl rearrangement, reductive elimination. When an acyl cyanide has a β-hydrogen, the intermediate cyanoalkylcarbonylpalladium (**15**) undergoes β-elimination to give alkenes.

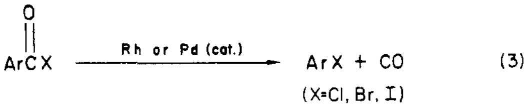
Acyl cyanides are an interesting class of compounds and have been utilized in a variety of synthetic transformations.[1] Although catalytic transformation of acyl cyanides is of interest in view of synthetic and mechanistic aspects, the reported reaction is limited to the nickel-catalyzed condensation reaction of benzoyl cyanide with pentane-2,4-dione.[2] We have found that acyl cyanides **1** undergo palladium-catalyzed decarbonylation under mild reaction conditions to give the corresponding nitriles **2** efficiently as depicted in eq 1.



$$\underset{\mathbf{1}}{\mathrm{R\overset{\overset{O}{\|}}{C}CN}} \xrightarrow{\mathrm{Pd(PPh_3)_4}} \underset{\mathbf{2}}{\mathrm{RCN}} + \mathrm{CO} \qquad (1)$$

The transition-metal-catalyzed decarbonylations of carbonyl compounds have been reported to proceed at elevated temperature.[3] Aldehydes undergo decarbonylation in the presence of rhodium and palladium catalysts to give hydrocarbons (eq 2).[4-6] Aromatic acyl halides (X = Cl,[4,7] Br,[4] I[8]) undergo similar decarbonylation (eq 3), while decarbonylation of the aliphatic acyl halides (X = Cl, Br) having a β-hydrogen gives olefins.[9] Blum et al. reported that aromatic acyl cyanides underwent decarbonylation using $RhCl(PPh_3)_3$ catalyst;[10] however, the decarbonylation required extremely drastic reaction conditions (300 °C) and the applicable substrates were limited to reactive acyl cyanides such as naphthoyl and *p*-chlorobenzoyl cyanides.

$$\mathrm{RCHO} \xrightarrow{\text{Rh or Pd (cat.)}} \mathrm{RH} + \mathrm{CO} \qquad (2)$$



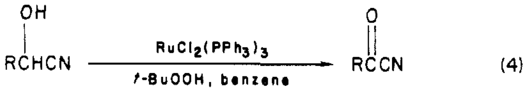
$$\mathrm{Ar\overset{\overset{O}{\|}}{C}X} \xrightarrow{\text{Rh or Pd (cat.)}} \underset{(\mathrm{X{=}Cl,\,Br,\,I})}{\mathrm{ArX} + \mathrm{CO}} \qquad (3)$$

Table I. Solvent Effect and Reaction Temperature on the Palladium-Catalyzed Decarbonylation of Benzoyl Cyanide[a]

entry	solvent	temp, °C	time, h	conversn,[b] %	yield[b] of benzonitrile, %
1	benzene	100	12	41	99
2	benzene	120	3	100	100
3	toluene	100	12	25	99
4	toluene	120	3	100	100
5	CH_3CN	120	3	61	100
6	THF	120	3	66	99
7	DMF	120	3	66	94
8	$CHCl_3$	120	3	29	52

[a] A mixture of benzoyl cyanide (1.0 mmol) and $Pd(PPh_3)_4$ (0.03 mmol) in a dry solvent (1.0 mL) was heated in a sealed tube. [b] Determined by GLC analysis based on benzoyl cyanide.

The present palladium-catalyzed decarbonylation proceeds with aromatic and heteroaromatic acyl cyanides generally at 120 °C. Since acyl cyanides are readily prepared by the ruthenium-catalyzed oxidation of cyanohydrins with *t*-BuOOH[11] (eq 4), the present decarbonylation reaction provides an efficient method for the conversion of aromatic and heteroaromatic aldehydes to the corresponding nitriles under mild and neutral conditions.



$$\mathrm{R\overset{\overset{OH}{|}}{C}HCN} \xrightarrow[t\text{-BuOOH, benzene}]{\mathrm{RuCl_2(PPh_3)_3}} \mathrm{R\overset{\overset{O}{\|}}{C}CN} \qquad (4)$$

Results and Discussion

The palladium-catalyzed decarbonylation of aromatic acyl cyanides proceeds at 120 °C, giving the corresponding nitriles. The catalytic activity of various metal complexes has been examined for the reaction of benzoyl cyanide at 120 °C. $Pd(PPh_3)_4$ is the best catalyst among the catalysts examined. $Pd(OAc)_2$–$2PPh_3$, $RuCl_3 \cdot nH_2O$, and $RuCl_2(PPh_3)_3$ gave unsatisfactory results. Using the well-known catalysts for the decarbonylation of aldehydes and acyl halides such as $RhCl(PPh_3)_3$,[10] $RhCl(CO)(PPh_3)_3$,[4] Pd–C (5%),[7,9] and $PdCl_2$,[9] benzonitrile could not be obtained, and the starting benzoyl cyanide was recovered. The results of the solvent effect for the above decarbonylation are summarized in Table I. The use of toluene and benzene gave satisfactory results. Upon heating at 120 °C, the reaction was completed within 3 h. When $CHCl_3$ was used, the conversion of benzoyl cyanide was low, giving a complex mixture of products.

Table II summarizes the representative results of the decarbonylation of acyl cyanides. Irrespective of the

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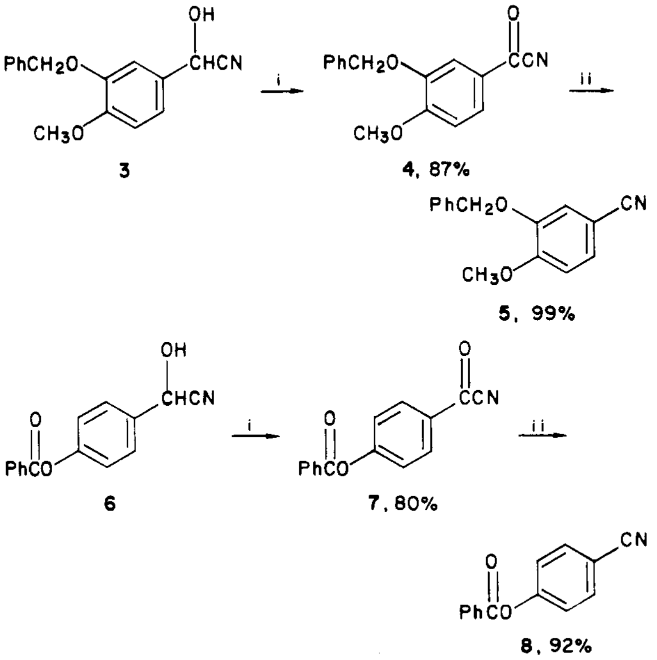
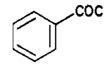
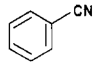
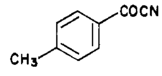
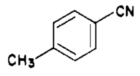
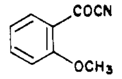
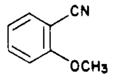
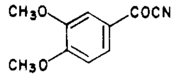
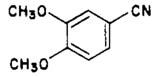
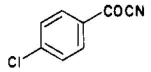
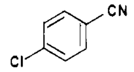
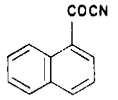
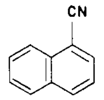
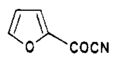
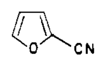
substituent on the aryl group, the acyl cyanides were obtained in excellent yields (entries 1–6). Heteroaromatic acyl cyanides also undergo the decarbonylation (entry 7).

Acyl cyanides are conveniently prepared by the ruthenium-catalyzed oxidation of cyanohydrins[11] which are readily prepared upon treatment of aldehydes with either $NaHSO_3$–KCN[12] or $(CH_3)_3SiCN/ZnI_2$–HCl.[13] Thus, the present reaction provides an efficient method for the conversion of aldehydes to the corresponding nitriles. Generally, nitriles have been prepared from aldehydes by the acid-induced dehydration of aldoximes.[14] Because the present reaction proceeds efficiently under mild and neutral conditions, the reactions is highly useful for the synthesis of acid-sensitive nitriles. The ruthenium-catalyzed oxidation of 3-(benzyloxy)-4-methoxybenzaldehyde cyanohydrin (**3**) with *t*-BuOOH gave the corresponding acyl cyanide **4** in 87% yield. The decarbonylation of **4** with $Pd(PPh_3)_4$ catalyst gave nitrile **5** in 99% yield. The similar treatment of 4-(benzoyloxy)benzaldehyde cyanohydrin (**6**) gave acyl cyanide **7** in 80% yield. The palladium-catalyzed reaction of **7** gave the corresponding nitrile **8** in 92% yield. In these reactions, benzyloxy and benzoyloxy groups are retained under the reaction conditions. Since acyl cyanides can be prepared by the reaction of acyl halides with metal cyanides[15] or trimethylsilyl cyanide,[16] the present reaction also provides a method for the synthesis of nitriles from carboxylic acids.



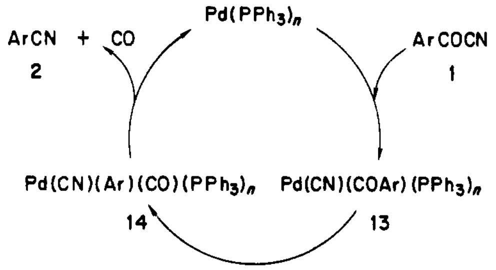
i, $RuCl_2(PPh_3)_3$-*t*-BuOOH, ii, $Pd(PPh_3)_4$

Table II. Palladium-Catalyzed Decarbonylation of Aromatic and Heteroaromatic Acyl Cyanides[a]

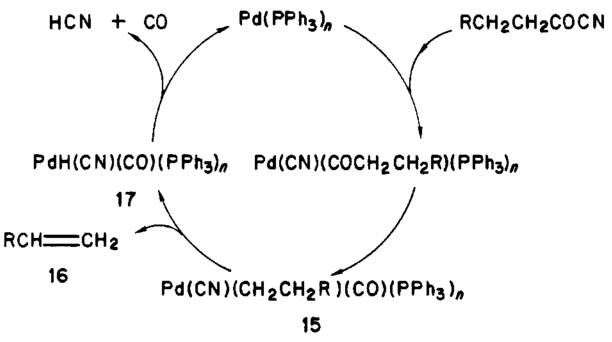
entry	acyl cyanide	product	yield,[b] %
1			100
2			97
3			96
4			97
5			98
6			94
7[c]			98

[a] A mixture of acyl cyanide (1.0 mmol) and $Pd(PPh_3)_4$ (0.03 mmol) in dry benzene (1.0 mL) was heated at 120 °C for 12 h. [b] Isolated yield. [c] The reaction was carried out without a solvent.

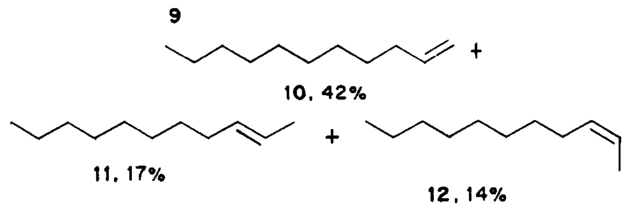
Scheme I



Scheme II



The decarbonylation of aliphatic acyl cyanides requires higher temperature (200 °C) to complete the reaction. Acyl cyanides bearing a β-hydrogen atom are converted into the corresponding olefins by the elimination of hydrogen cyanide. Treatment of lauroyl cyanide (**9**) with $Pd(PPh_3)_4$ at 200 °C gave 1-undecene (**10**, 42%), *trans*-2-undecene (**11**, 17%), and *cis*-2-undecene (**12**, 14%).



The palladium-catalyzed decarbonylation can be rationalized by assuming the pathway shown in Scheme I,

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which is quite similar to the mechanism for the decarbonylation of acyl halides and aldehydes.[17,18] The acyl cyanide undergoes the oxidative addition to $Pd(PPh_3)_4$ to give cyanoacylpalladium complex **13**. Acyl–aryl rearrangement gives cyanoarylcarbonylpalladium complex **14**. Reductive elimination of **14** gives aryl cyanide and $Pd(CO)(PPh_3)_n$, which undergoes dissociation of carbon monoxide. Alternatively, the complex **14** undergoes dissociation of CO to give $Pd(CN)(Ar)(PPh_3)_n$, which undergoes reductive coupling to give ArCN and $Pd(PPh_3)_n$. When the acyl cyanide has a β-hydrogen, the intermediate cyanoalkylcarbonylpalladium complex **15**, which corresponds to the complex **14**, undergoes β-elimination to give alkenes **16** and hydridocyanopalladium complex **17**. Again, reductive coupling of **17** gives hydrogen cyanide, carbon monoxide, and Pd(0) catalyst to complete the catalytic cycle as shown in Scheme II. The β-elimination of [PdH] species proceeds much faster than the reductive coupling to form alkyl cyanides. The isomerization of the carbon–carbon double bonds may proceed by the addition–elimination of [PdH] species. The intermediacy of the cyanoacylpalladium complex **13** has been indicated in the palladium-catalyzed reaction of aryl iodides with KCN in the presence of carbon monoxide.[19] Stoichiometric reaction of benzoyl cyanide with $Pd(PPh_3)_4$ in benzene at room temperature gave a yellow palladium complex. The IR spectrum of the complex shows the absorptions at 2125 and 1620 cm^{-1}, which correspond to the C≡N and the C=O stretchings, respectively. The parent benzoyl cyanide shows the C≡N and C=O absorptions at 2225 and 1680 cm^{-1}, respectively. Apparently, the C=O absorption appears in the region of the C=O absorptions for the metal–acyl bonds,[20] indicating the $Pd(CN)(COC_6H_5)(PPh_3)_n$ structure. It is reported that the stoichiometric reaction of *trans*-stilbenebis(triphenylphosphine)platinum(0) with benzoyl cyanide gave $Pt(CN)(COC_6H_5)(PPh_3)_2$.[21] The first step of the present reaction seems to be the oxidative addition of benzoyl cyanide to $Pd(PPh_3)_4$. The pyrolysis of the yellow complex in benzene at reflux gave benzonitrile. The reductive elimination of $Pd(CN)(C_6H_5)(PPh_3)_n$ complex (**14**) to give benzonitrile corresponds to the key step in the palladium-catalyzed cyanation of aryl iodides with KCN.[22] The palladium-catalyzed decarbonylation of aroyl halides requires high reaction temperatures (265–360 °C).[7] This is due to the difficulty of the reductive elimination of the arylhalopalladium complexes. The low reaction temperature of the present decarbonylation is due to the easy reductive coupling of the arylcyanopalladium complex. In the catalytic decarbonylation of aldehydes and acyl halides, the aroylrhodium[23] and arylpalladium complexes[24] have been trapped by the reactions with alkenes. However, the palladium-catalyzed reaction of benzoyl cyanide in the presence of either ethyl acrylate or styrene gave neither the arylation nor aroylation products, and only benzonitrile was obtained. These results are also consistent with the easy reductive coupling of the arylcyanopalladium complexes.

Experimental Section

All melting points are uncorrected. IR spectra were recorded on a Hitachi 215 spectrometer. ^{1}H NMR spectra were obtained on a 60-MHz Model JNM-PMX-60 SI (JEOL) spectrometer, and chemical shifts were expressed in parts per million downfield from Me_4Si. GLC analyses were carried out on a JEOL JGC-20-KFP by using a 1-m analytical column packed with Silicone SE-30 on Uniport and on a Shimadzu GC-MINI 2 with a CLH-M2 column holder by using a SCOT OV-17 glass capillary column (0.3 mm × 30 m). Mass spectra were obtained on a Hitachi RMS-4 mass spectrometer. Elemental analyses were performed on a Yanagimoto MT-2 CHN corder.

Materials. Benzene and toluene were distilled over benzophenone ketyl under argon atmosphere. Tetrakis(triphenylphosphine)palladium[25] and dichlorotris(triphenylphosphine)ruthenium[26] were prepared by the literature procedures. Anhydrous solution of *t*-BuOOH in benzene was prepared and titrated by using the Sharpless method.[27]

Acyl Cyanides. Aromatic and heteroaromatic acyl cyanides were prepared by the ruthenium-catalyzed oxidation of the corresponding cyanohydrins with *tert*-butyl hydroperoxide.[11] Cyanohydrins were prepared by the reaction of aldehydes with potassium cyanide[12] or with trimethylsilyl cyanide.[13] Lauroyl cyanide (**9**) was prepared by the reaction of lauroyl chloride with trimethylsilyl cyanide.[16]

3-(Benzyloxy)-4-methoxybenzoyl Cyanide (4). A 30-mL round-bottomed flask equipped with a magnetic stirring bar and a pressure equalizing dropping funnel connected to a three-way stopcock was charged with 3-(benzyloxy)-4-methoxybenzaldehyde cyanohydrin (**3**) (0.403 g, 1.50 mmol), $RuCl_2(PPh_3)_3$ (0.072 g, 0.075 mmol), and dry benzene (3.0 mL) under argon atmosphere. To the mixture was added a 3.38 M solution of *t*-BuOOH in dry benzene (0.89 mL, 3.0 mmol) dropwise at room temperature over a period of 1 h. After additional stirring for 3 h, palladium black was added to decompose excess *t*-BuOOH. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (6 g of Florisil). Elution with ether (60 mL) afforded **4** (0.346 g, 87%) as a pale yellow solid. Recrystallization from hexane gave yellow microcrystals: mp 101.5–102.5 °C; IR (Nujol) 2225 (CN), 1670 (C=O), 1600, 1590, 1530, 1310, 1295, 1265, 1225, 1155, 1015, 885, 815 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 3.97 (s, 3 H, OCH_3), 5.15 (s, 2 H, $-CH_2O-$), 6.97 (d, $J = 8$ Hz, 1 H), 7.25–7.50 (m, 5 H), 7.53 (d, $J = 2$ Hz, 1 H), 7.80 (dd, $J = 8, 2$ Hz, 1 H). Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.88; H, 4.90; N, 5.19.

Palladium-Catalyzed Decarbonylation of Acyl Cyanide 4. A mixture of **4** (0.267 g, 1.00 mmol) and $Pd(PPh_3)_4$ (0.036 g, 0.03 mmol) in dry toluene (1.0 mL) was heated at 120 °C for 6 h in a sealed Pyrex tube (150 mm × 15 mm) under argon atmosphere. After evaporation of the solvent the residue was subjected to column chromatography (5 g of silica gel). Elution with a mixture of ether and hexane (1:1, 60 mL) gave 3-(benzyloxy)-4-methoxybenzonitrile (**5**) (0.237 g, 99%) as a colorless solid. Recrystallization from ether–hexane (1:4) gave colorless needles: mp 73.0–73.5 °C; IR (Nujol) 2220 (CN), 1580, 1270, 1240, 1130, 1005, 845, 810, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 3.90 (s, 3 H, OCH_3), 5.10 (s, 2 H, $-CH_2O-$), 6.87 (d, $J = 8$ Hz, 1 H), 7.07 (d, $J = 2$ Hz, 1 H), 7.25 (dd, $J = 8, 2$ Hz, 1 H), 7.28–7.43 (m, 5 H). Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.31; H, 5.45; N, 5.69.

Preparation of 4-(Benzoyloxy)benzoyl Cyanide (7). A 100-mL round-bottomed flask equipped with a magnetic stirring bar and a pressure equalizing dropping funnel connected to a

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three-way stopcock was charged with 4-(benzoyloxy)benzaldehyde cyanohydrin (**6**) (5.07 g, 20.2 mmol), $RuCl_2(PPh_3)_3$ (0.579 g, 0.604 mmol), and dry benzene (60 mL) under an argon atmosphere. The mixture was stirred at room temperature and a 1.75 M solution of *t*-BuOOH in dry benzene (23 mL, 40 mmol) was added dropwise over a period of 5 h. After additional stirring for 5 h, $NaHSO_3$ (10 g) was added to decompose excess *t*-BuOOH. After filtration, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography (30 g of Florisil). Elution with a mixture of ether and hexane (1:1) afforded **7** (4.02 g, 80%) as a colorless solid. Recrystallization from dry CH_2Cl_2–hexane gave microcrystals: mp 117.5–118.5 °C; IR (Nujol) 2220 (CN), 1740 (C=O), 1660 (C=O), 1590, 1250, 1210, 1160, 1050, 1020, 970, 880 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 7.23–7.70 (m, 3 H), 7.40 (d, J = 8.5 Hz, 2 H), 8.00–8.30 (m, 2 H), 8.13 (d, J = 8.5 Hz, 2 H). Anal. Calcd for $C_{15}H_9NO_3$: C, 71.71; H, 3.61; N, 5.58. Found: C, 71.75; H, 3.52; N, 5.46.

Palladium-Catalyzed Decarbonylation of 7. A mixture of **7** (0.251 g, 1.00 mmol) and $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol) in dry toluene (1.0 mL) was heated at 120 °C for 6 h in a sealed Pyrex tube under an argon atmosphere. After evaporation of the solvent, the residue was purified by preparative TLC (silica gel). Elution with a mixture of ether and hexane (1:1) gave 4-cyanophenyl benzoate (**8**) (0.206 g, 92%) as a colorless solid. Recrystallization from ether gave colorless needles: mp 92.5–93.5 °C; IR (Nujol) 2240 (CN), 1725 (C=O), 1605, 1260, 1215, 1170, 1055, 1020, 880, 815, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 60 Hz) δ 7.25 (d, J = 9 Hz, 2 H), 7.37–7.72 (m, 3 H), 7.65 (d, J = 9 Hz, 2 H), 8.08 (dd, J = 8, 2 Hz, 2 H). Anal. Calcd for $C_{14}H_9NO_2$: C, 75.33; H, 4.06; N, 6.28. Found: C, 75.34; H, 3.99; N, 6.16.

General Procedure for the Palladium-Catalyzed Decarbonylation of Aromatic Acyl Cyanides. A mixture of acyl cyanide (1.0 mmol) and $Pd(PPh_3)_4$ (0.03 mmol) in dry benzene (1.0 mL) was heated at 120 °C for 12 h in a sealed Pyrex tube (150 mm × 15 mm) under an argon atmosphere. After evaporation of the solvent, the residue was subjected to column chromatography (5 g of silica gel). Elution with a mixture of ether and hexane (1:1) gave the corresponding nitrile.

4-Methylbenzonitrile: IR (neat) 2940, 2230 (CN), 1790, 1610, 1510, 1180, 1040, 820 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 2.40 (s, 3 H, CH_3), 7.20 (d, J = 8 Hz, 2 H, PhH), 7.48 (d, J = 8 Hz, 2 H, PhH); mass spectrum, *m/e* (relative intensity) 117 (M^+, 90), 116 (60), 91 (M^+ – CN, 30), 90 (30), 89 (70), 64 (65), 63 (100), 62 (53), 61 (56), 51 (64), 50 (64).

2-Methoxybenzonitrile: IR (neat) 2950, 2855, 2240 (CN), 1605, 1590, 1500, 1470, 1440, 1295, 1265, 1170, 1115, 1050, 1020, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.92 (s, 3 H, OCH_3), 6.77–7.17 (m, 2 H, PhH), 7.33–7.70 (m, 2 H, PhH); mass spectrum, *m/e* (relative intensity) 133 (M^+, 30), 105 (100), 104 (91), 90 (97), 79 (39), 78 (21), 77 (36), 76 (36), 64 (73), 63 (79). Anal. Calcd for C_8H_7NO: C, 72.17; H, 5.30; N, 10.52. Found: C, 71.82; H, 5.32; N, 10.14.

3,4-Dimethoxybenzonitrile: mp 63.0–63.5 °C; IR (Nujol) 2225 (CN), 1605, 1520, 1420, 1275, 1250, 1160, 1140, 1020, 880, 810 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.87 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 6.85 (d, J = 9 Hz, 1 H), 7.03 (d, J = 2 Hz, 1 H), 7.26 (dd, J = 2, 9 Hz, 1 H). Anal. Calcd for $C_9H_9NO_3$: C, 66.24; H, 5.56; N, 8.58. Found: C, 66.40; H, 5.58; N, 8.52.

4-Chlorobenzonitrile: mp 90.5–91.5 °C; IR (Nujol) 2230 (CN), 1595, 1090, 1015, 825 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 7.37 (d, J = 8 Hz, 2 H), 7.55 (d, J = 8 Hz, 2 H). Anal. Calcd for C_7H_4NCl: C, 61.12; H, 2.93; N, 10.18. Found: C, 61.22; H, 2.88; N, 10.27.

1-Naphthonitrile: IR (neat) 3070, 2225 (CN), 1730, 1595, 1515, 1380, 1345, 1220, 1120, 1060, 800, 770 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 7.25–8.38 (m, 7 H, Ar H); mass spectrum, *m/e* (relative intensity) 154 (M^+ + 1, 15), 153 (M^+, 100), 152 (M^+ – 1, 9), 127 (M^+ – CN, 15), 126 (33), 76 (15), 75 (22), 74 (20), 63 (17), 51 (16), 50 (20), 28 (40). Anal. Calcd for $C_{11}H_7N$: C, 86.25; H, 4.61; N, 9.14. Found: C, 86.54; H, 4.52; N, 9.00.

2-Cyanofuran. A mixture of 2-furoyl cyanide (0.385 g, 3.18 mmol) and $Pd(PPh_3)_4$ (0.037 g, 0.032 mmol) was heated at 120 °C for 12 h in a sealed Pyrex tube under an argon atmosphere. Distillation of the mixture gave 2-cyanofuran (0.289 g, 98%) as a pale yellow liquid: bp 180–230 °C (Kugelrohr); IR (neat) 3140, 2230 (CN), 1650, 1560, 1450, 1390, 1305, 1285, 1240, 1160, 1080, 1030, 995, 900, 880, 770, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 6.73 (dd, J = 3.6, 1.6 Hz, 1 H), 7.62 (d, J = 3.6 Hz, 1 H), 7.85 (d, J = 1.6 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 95 (M^+ + 2, 15), 93 (M^+, 5), 54 (54), 39 (96), 38 (100), 37 (96).

Palladium-Catalyzed Reaction of Lauroyl Cyanide (9). A mixture of **9** (0.322 g, 1.54 mmol) and $Pd(PPh_3)_4$ (0.053 g, 0.046 mmol) in dry benzene (1.5 mL) was heated at 200 °C for 12 h in a sealed tube under argon. After evaporation of the solvent, the residue was purified by column chromatography (5 g of silica gel, hexane) to give an isomeric mixture of undecenes (0.173 g, 73%). Anal. Calcd for $C_{11}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.75; H, 14.27. The GLC analyses (using a 30-m glass capillary column packed with Silicone OV-17) showed that the mixture consisted of 1-undecene (**10**, 42%), *trans*-2-undecene (**11**, 17%), and *cis*-2-undecene (**12**, 14%). The structures of these compounds were determined by the comparison of the spectral data with those of authentic samples.[28]

Stoichiometric Reaction of Benzoyl Cyanide with $Pd(PPh_3)_4$. A solution of benzoyl cyanide (0.041 g, 0.31 mmol) and $Pd(PPh_3)_4$ (0.230 g, 0.20 mmol) in dry benzene (17 mL) was stirred overnight at room temperature under an argon atmosphere. After evaporation of the solvent, the residual solid was washed with dry and degassed hexane (10 mL × 3). Evaporation of the solvent gave an air-sensitive palladium complex, $Pd(CN)(COPh)(PPh_3)_2$ (**13**) (0.153 g, 89%): IR (Nujol) 2125 (CN), 1620 (CO), 1435, 1180, 1150, 1095, 995, 870, 745, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 7.07–7.90 (m).

Pyrolysis of the Benzoylpalladium Complex 13. A solution of cyanobenzoylbis(triphenylphosphine)palladium **13** (0.100 g, 0.13 mmol) in dry benzene (10 mL) was refluxed for 3 h under an argon atmosphere. The mixture was passed through a Florisil short column. GLC analysis of the eluate showed that benzonitrile was obtained in 80% yield.

Palladium-Catalyzed Reaction of Benzoyl Cyanide with Olefins. A mixture of benzoyl cyanide (0.131 g, 1.00 mmol), ethyl acrylate (0.100 g, 1.00 mmol), and $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol) in dry toluene (1.0 mL) was heated at 60–120 °C for 6 h in a sealed tube under argon. GLC analysis of the reaction mixture showed that ethyl acrylate was remained unreacted and only decarbonylation product benzonitrile was obtained in 20–60% yield. The same reaction of benzoyl cyanide with styrene (0.104 g, 1.00 mmol) gave similar results.

Registry No. **3**, 67387-77-3; **4**, 97798-37-3; **5**, 52805-37-5; **6**, 100207-69-0; **7**, 100207-70-3; **8**, 16513-72-7; **9**, 100207-71-4; **10**, 821-95-4; **11**, 693-61-8; **12**, 821-96-5; **13**, 100229-27-4; Pd $(PPh_3)_4$, 14221-01-3; $RuCl_2(PPh_3)_3$, 15529-49-4; benzoyl cyanide, 613-90-1; *p*-methylbenzoyl cyanide, 14271-73-9; *o*-methoxybenzoyl cyanide, 72371-46-1; 3,4-dimethoxybenzoyl cyanide, 65961-86-6; *p*-chlorobenzoyl cyanide, 13014-48-7; naphthoyl cyanide, 14271-86-4; 2-furoyl cyanide, 6047-91-2; benzonitrile, 100-47-0; 4-methylbenzonitrile, 104-85-8; 2-methoxybenzonitrile, 6609-56-9; 3,4-dimethoxybenzonitrile, 2024-83-1; 4-chlorobenzonitrile, 623-03-0; 1-naphthonitrile, 86-53-3; 2-cyanofuran, 617-90-3.

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