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Palladium Catalyzed Cyanocarbonylation of Organic Iodides

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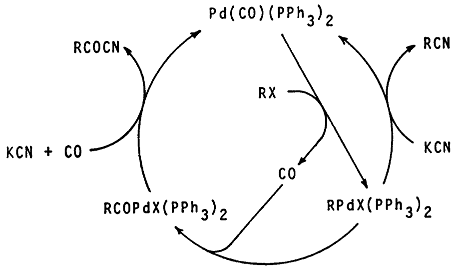
Synopsis. Palladium complex catalyzed carbonylation of aromatic and heteroaromatic iodides in the presence of potassium cyanide gave aroyl cyanides in fair to excellent yields, offering the first example of cyanocarbonylation.

Palladium complex catalyzed carbonylation of organic halides has been successfully performed, but limited to synthesis of carboxylic acids and their derivatives such as esters, aldehydes, and amides.1) We have recently found that ketones are formed in excellent yield when the reaction was run with organotin compounds.2) In the catalytic cycle of this reaction, an electrophilic attack of an acyl-palladium intermediate on an organotin compound is postulated. As a continuation of halide carbonylation with carbon nucleophiles, we tried the reaction with potassium cyanide. This paper describes the results of this entirely new carbonylation, namely, cyanocarbonylation of halides.

$$\text{R-X} + \text{CO} + \text{KCN} \longrightarrow \text{R-CO-CN} + \text{KX}$$

The cyanocarbonylation was effected using a palladium complex, $C_6H_5PdI[P(C_6H_5)_3]_2$, as a catalyst precursor. This complex is believed to be an intermediate in other carbonylation reactions of organic halides by palladium complex catalysts.3) Aromatic and heteroaromatic iodides were smoothly carbonylated in the presence of potassium cyanide to give aroyl cyanide in fair to excellent yields. Nitriles were generally formed as by-products, but the amount was negligible except the iodothiophene reaction. The catalysis of this reaction was quite sensitive to the ratio of potassium cyanide to the palladium complex. At a much higher ratio than that specified in Table 1 for each halide, the reaction did not work well. This may be connected with poisoning effect of cyanide ion4) which makes the palladium catalyst inactive. The extent of poisoning seemed to be very dependent on the structure of halides. Thus, the yield of aroyl or acyl cyanide from ethyl *p*-iodobenzoate, *p*-dibromobenzene, *p*-bromoacetophenone, *β*-bromostyrene, and benzyl chloride was some 10% at best or even below under the analogous reaction conditions. This may be because of diminishing catalytic activity due to poisoning which eventually led to the cease of catalysis.5) Hopefully, the poisoning problem will be solved by a slow addition of potassium cyanide to the reaction system as Cassar and co-workers did for nickel-catalyzed cyanation of aromatic halides.6)



Scheme 1.

The cyanocarbonylation can be accounted for by the mechanism outlined in scheme 1.3) Oxidative addition of an iodide to the palladium(0) complex affords an aryl-palladium intermediate which is then transformed into an aroyl-palladium species through CO insertion. Electrophilic attack of potassium cyanide on the aroyl moiety of the latter species would give aroyl cyanide, regenerating the palladium(0) species. Another possibility would be displacement of iodide from the aroyl-palladium-iodide complex by cyanide. The aroyl-palladium-cyanide complex thus formed would undergo reductive elimination to give aroyl cyanide and the palladium(0) catalyst.

In summary, a novel aroyl cyanide synthesis occurs by carbonylation of aryl iodides with potassium cyanide. This paper offers another useful variation of halide carbonylation.

Experimental

Melting points were determined using a Yanagimoto hot-stage apparatus and are uncorrected. PMR and IR spectra were recorded on a Hitachi R-40 and JASCO A-302 spectrometers, respectively. Tetrahydrofuran was dried and purified by the standard techniques. Iodophenylbis(triphenylphosphine)palladium8) and 2-iodothiophene9) were prepared by the published methods. Other halides were purchased and purified before use.

Carbonylation of Iodobenzene. General Procedures: A 27 ml stainless steel autoclave was charged with iodophenylbis(triphenylphosphine)palladium (20.9 mg, 2.5×10^{-2} mmol),

TABLE 1. CYANOCARBONYLATION OF ORGANIC HALIDES[a)]

RX mmol	KCN mmol	Amount of solvent/ml	P_{CO} atm	Time h	RCOCN[b)] (%)	RCN[b)] (%)
C_6H_5I (7.5)	3.75	1.5	20	20	91 (83)	1.4
C_6H_5I (3.75)	3.98	1.5	20	19	48	1.7
p-$CH_3OC_6H_4I$ (7.5)	3.75	1.5	20	15	92 (88)	1.1
p-$CH_3C_6H_4I$ (5.63)	1.88	0.75	8	18	69 (64)	2.5
2-C_4H_3SI (2.82)	0.94	0.5	8	24	45	22.0

a) 100 °C, $PhPdI(PPh_3)_2=2.5\times10^{-2}$ mmol, tetrahydrofuran solvent. b) Estimated by GLC analysis using internal standard. Yields for isolated samples are shown in parentheses. c) 2-Thienyl iodide.

dry potassium cyanide powder (245 mg, 3.75 mmol), iodobenzene (0.84 ml, 7.5 mmol), and 1.5 ml of tetrahydrofuran. Carbon monoxide was introduced at 20 atm. The mixture was stirred at 100 °C overnight, diluted with ether, and was filtered. The solvent was evaporated. The residue was subjected to chromatography through a short silica gel column, iodobenzene being first eluted by hexane followed by benzoyl cyanide eluted by benzene, 410 mg, 83.2%. A short-path distillation gave an analytical sample, mp 33.0—34.0 °C. PMR ($CDCl_3$) δ 7.45—8.30 (aromatic). IR (melt) 2220 (ν_{CN}) and 1677 cm^{-1} (ν_{CO}). Found: C, 73.24; H, 3.91%. Calcd for C_8H_5NO: C, 73.27; H, 3.91%.

Melting points, spectral, and analytical data for other aroyl cyanides were as follows.

p-*Methoxybenzoyl Cyanide*: Mp 58.1—59.0 °C. PMR ($CDCl_3$) δ 3.99 (3H, s, CH_3), 7.10 (2H, d, J=9 Hz, meta protons), and 8.16 (2H, d, ortho protons). IR (nujol) 2220 (ν_{CN}) and 1675 cm^{-1} (ν_{CO}). Found: C, 67.06; H, 4.37%. Calcd for $C_9H_7NO_2$: C, 67.08; H, 4.38%.

p-*Methylbenzoyl Cyanide*: Mp 49.5—50.0 °C. PMR ($CDCl_3$) δ 2.53 (3H, s, CH_3), 7.45 (2H, d, J=8 Hz, meta protons), and 8.11 (2H, d, ortho protons). IR (melt) 2225 (ν_{CN}) and 1670 cm^{-1} (ν_{CO}). Found: C, 74.31; H, 4.84%. Calcd for C_9H_7NO: C, 74.47; H, 4.86%.

2-Thenoyl Cyanide: Mp 53.1—54.6 °C. PMR ($CDCl_3$) δ 7.25—7.43 (1H, m, 4-position) and 7.93—8.22 (2H, m, 3- and 5-positions). IR (melt) 2220 (ν_{CN}) and 1648 cm^{-1} (ν_{CO}). Found: C, 52.55; H, 2.31%. Calcd for C_6H_3NOS: C, 52.54; H, 2.20%.

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References

1) A. Schoenberg and R. F. Heck, *J. Am. Chem. Soc.*, **96**, 7761 (1974); A. Schoenberg, I. Bartoletti, and R. F. Heck, *J. Org. Chem.*, **39**, 3318 (1974); A. Schoenberg and R. F. Heck, *ibid.*, **39**, 3327 (1974); J. K. Stille and P. K. Wong, *ibid.*, **40**, 532 (1975); M. Hidai, T. Hikita, Y. Wada, Y. Fujikura, and Y. Uchida, *Bull. Chem. Soc. Jpn.*, **48**, 2075 (1975); L. Cassar, M. Foà, and A. Gardano, *J. Organometal. Chem.*, **121**, C55 (1976).

2) M. Tanaka, *Tetrahedron Lett.*, **1979**, 2601.

3) For the mechanism of halide carbonylation reactions in the presence of palladium complex catalysts, see P. E. Garrou and R. F. Heck, *J. Am. Chem. Soc.*, **98**, 4115 (1976).

4) A similar effect of cyanide ion on the nickel or palladium complex catalyzed cyanation of aromatic halides has been reported. See the Refs. 6 and 7.

5) From a β-bromostyrene reaction where the catalytic activity had completely lost at the early stage, a palladium complex which exhibited a ν_{CN} band at 2140 cm^{-1} could be recovered. Its structure has not been studied in detail.

6) L. Cassar, S. Ferrara, and M. Foà, *Adv. Chem. Ser.*, **132**, 252 (1974).

7) K. Takagi, T. Okamoto, Y. Sakakibara, A. Ohno, S. Oka, and N. Hayama, *Bull. Chem. Soc. Jpn.*, **49**, 3177 (1976).

8) P. Fitton and E. A. Rick, *J. Organometal. Chem.*, **28**, 287 (1971).

9) *Org. Synth.*, Coll. Vol. II, 357 (1943).