February, 1989] © *1989 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,* ***62,*** *605—607 (1989)* 605

The Reaction of Arylazo Aryl Sulfones with Carbon Monoxide and Nucleophiles Catalyzed by the Palladium(0) Complex[1)]

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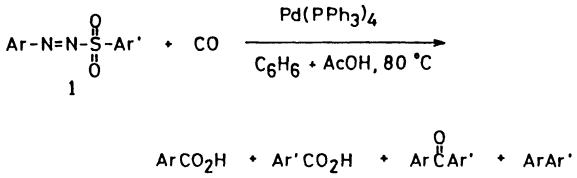
(Received June 29, 1988)

Synopsis. The reaction of arylazo aryl sulfone (**1**) with carbon monoxide in the presence of the palladium(0) catalyst affords substituted benzoic acid in a good yield, together with minor yields of diaryl ketone and biaryl. The reactions of **1** with carbon monoxide and such nucleophiles as alcohols and amines under similar conditions give esters and amides, respectively.

Arylpalladium reagents obtained from aryl halides or arylmercurials have been utilized extensively for the arylation of olefins.[2)] Kikukawa et al. reported that arylpalladium species was also formed from arenediazonium salts[3)] or *N*-nitrosoacetanilide[4)] catalyzed by palladium complexes to arylate olefins in high yields. Recently, we reported the reaction of arylazo aryl sulfones with olefins catalyzed by the palladium(0) complex to give aryl olefins in a high yield, and a diarylpalladium(II) species was proposed as an intermediate.[5)] If such an intermediate participates in this reaction, the insertion of carbon monoxide into the carbon–metal σ-bond and the resulting carbonylated products can be expected, since a number of reactions of organometallics with carbon monoxide have been reported.[6)] We studied the reactions of arylazo aryl sulfone with carbon monoxide and nucleophiles catalyzed by the palladium(0) complex in order to clarify the formation of a diarylpalladium(II) intermediate by obtaining carbonylated products, and the results are described herein.

When carbon monoxide was passed through, with bubbling, into a solution of phenylazo *p*-tolyl sulfone (**1a**) in benzene and acetic acid, benzoic acid (35%), *p*-methylbenzoic acid (37%), *p*-methylbenzophenone (1%), and *p*-methylbiphenyl (6%) were obtained. Similarly, *p*-tolylazo phenyl sulfone (**1b**) afforded benzoic acid (42%), *p*-methylbenzoic acid (34%), 4-methylbenzophenone (1%), and *p*-methylbiphenyl (3%) under similar reaction conditions. When the two aryl groups of **1** are the same (**1c**: Ar=Ar′=Ph, **1d**: Ar=Ar′=*p*-Tol, and **1e**: Ar=Ar′=*p*-$MeOC_6H_4$), sole benzoic acid or substituted benzoic acid was formed in a good yield. The results are summarized in Table 1. It is of interest that almost equal amounts of benzoic acid and *p*-methylbenzoic acid were obtained, respectively, from the reactions of the azosulfone **1a** and **1b** with carbon monoxide catalyzed by the palladium(0) complex; these results suggest the formation of an intermediate, such as diarylpalladium(II), having an equal reactivity toward carbon monoxide, as we proposed previously.[5)]



At first, we expected that diaryl ketone (ArCOAr′) would be formed as a major product; however, such a compound was obtained in a yield of only a few percent, and instead, carboxylic acid was formed in a good yield. The formation of benzoic acids may be attributed by the reaction of diarylpalladium(II) species with a carbon dioxide contaminated impurity in the carbon monoxide gas, similar to the reaction of a Grignard reagent and carbon dioxide. The reaction of **1c** with carbon dioxide was carried out in the presence of the palladium(0) complex under similar conditions. However no benzoic acid was detected in the reaction mixtures. Thus, the possibility of the formation of benzoic acids by the reaction of diarylpalladium(II) species with carbon dioxide can be excluded.

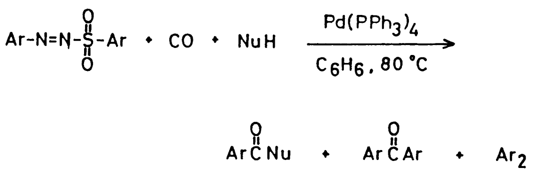
Then, we considered that the carboxylic acid was formed by the nucleophilic reaction of water, a contaminated impurity in carbon monoxide gas, and unremovable moisture in the reaction equipment, with the (arylcarbonyl)arylpalladium(II) species which had been formed by the insertion of carbon monoxide into the diarylpalladium(II) species. If this reaction path is real, the formation of esters or amides can be expected when the palladium(0)-catalyzed reaction of **1**

Table 1. Reaction of Arylazo Aryl Sulfone (**1**) with Carbon Monoxide Catalyzed by Tetrakis(triphenylphosphine)palladium(0)

	Ar and Ar′ in **1**		Products, Yield[a)]/%			
	Ar	Ar′	$ArCO_2H$	$Ar'CO_2H$	ArCOAr′	ArAr′
1a	Ph	*p*-Tol	35	37	1	6
1b	*p*-Tol	Ph	34	42	1	3
1c	Ph	Ph	76[b)]	—	2	5
1d	*p*-Tol	*p*-Tol	78[b)]	—	1	4
1e	*p*-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	72[b)]	—	1	5

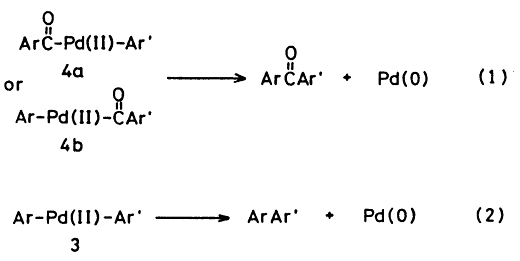
a) The yields were determined by means of GC. b) This value includes the yield of $Ar'CO_2H$, since the products, $ArCO_2H$ and $Ar'CO_2H$, are identical when the Ar and Ar′ groups in **1** are the same.

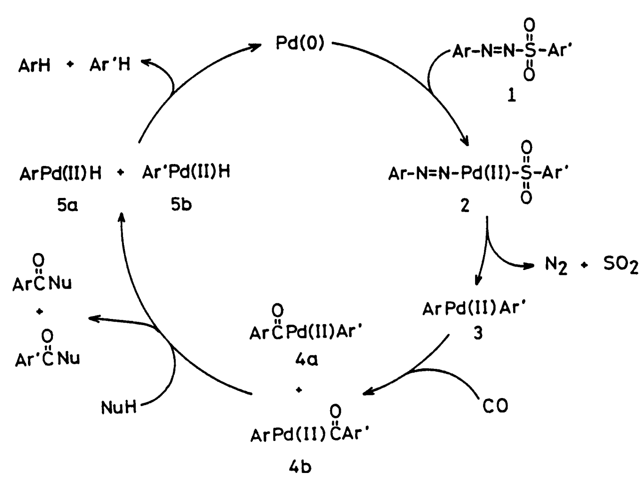
is carried out in the presence of such nucleophiles as alcohols or amines. The reaction of **1c** catalyzed by the palladium(0) complex was carried out in benzene-methanol at 80 °C. As we expected, methyl benzoate was formed, although the yield was not so high; no benzoic acid was detected in this case. Similarly, the reaction of azosulfone **1** with such nucleophiles as ethanol, sodium methoxide, and amines under similar conditions gave the corresponding esters and amides in moderate yields. However, the reaction of **1c** with sodium acetate did not give acetylbenzoate or phenylbenzoate. The acetate ion may not have enough nucleophilicity to react with (arylcarbonyl)arylpalladium(II) species. The results are summarized in Table 2. These findings support our consideration of the formation of the diarylpalladium(II) species which is carbonylated by carbon monoxide to form arylcarbonyl aryl palladium(II) species and a subsequent reaction with nucleophiles to give the final product.



The palladium(II)-catalyzed reaction of arylazo aryl sulfones with carbon monoxide and nucleophiles is accounted for by Scheme 1, involving the oxidative addition of **1** to the palladium(0) catalyst to give the adduct **2**, which then extrudes nitrogen and sulfur dioxide to give the diarylpalladium(II) species (**3**). Carbon monoxide inserts into the palladium-carbon bond of the intermediate **3** to give (arylcarbonyl)arylpalladium(II) (**4**), which degrades to the corrsponding carboxylic acid derivatives and arylhydridopalladium(II) (**5**) upon the reaction with the nucleophiles. The reductive elimination of arene from **5** gives palladium(0), and thus the catalytic cycle is achieved.

The reason why the formation of benzophenone derivatives is minor may be attributed to the reaction of the (arylcarbonyl)arylpalladium(II) species with the nucleophiles to give benzoic acids or their esters and amides is faster than the reductive elimination of benzophenone derivatives from **4**,[7] (Eq. 1). The formation of biary may be accounted for by the reductive elimination from diarylpalladium(II) before which is carbonylated by carbon monoxide (Eq. 2).





Scheme 1.

Table 2. Reaction of Azosulfone (**1**) with Carbon Monoxide and Nucleophiles Catalyzed by Tetrakis(triphenylphosphine)plladium(0)[a]

Azosulfone	Nucleophile	Product, Yield[b]/%	
1c	MeOH	$PhCO_2Me$	28
1c	EtOH	$PhCO_2Et$	35
1c	MeONa	$PhCO_2Me$	55
1d	MeONa	p-$CH_3C_6H_4CO_2Me$	54
1e	MeONa	p-$CH_3OC_6H_4CO_2Me$	50
1c	$PhNH_2$	PhCONHPh	59
1c	Et_2NH	$PhNEt_2$	57
1c	AcONa	$PhCO_2Ac$	0

a) Diaryl ketone (Ar_2CO; 1—2%) and biaryl (Ar_2; 4—10%) were formed in all cases. b) The yields were determined by means of GC.

Experimental

Measurement. The melting points and boiling points are uncorrected. The infrared absorption spectra were determined on a Hitachi Model 260-10 spectrophotometer, using samples as either neat liquid or in KBr disks. The ^{1}H NMR spectra were recorded at 60 MHz by using a JNM-PMX 60 SI spectrometer, with tetramethylsilane as the internal standard in $CDCl_3$. The mass spectra were determined with a JEOL JMS-DX 300 mass spectrometer with the JEOL JMA-5000 Mass Data System at an ionizing voltage of 20—70 eV. The gas chromatography was carried out with Hitachi Models 163 and 263-30 gas chromatographs using a 1 m column packed with 10% SE-30. The gel-permeation chromatography was performed by using a JAI LC-08 liquid chromatograph with a JAIGEL column (20ϕX600 mmX2, with chloroform as an eluent).

Materials. All the solvents were distilled and stored under nitrogen. Palladium chloride of Wako Chemicals was used without further purification. Tetrakis(triphenylphosphine)palladium(0) was prepared by the method described in the literature.[8] Phenylazo p-tolyl sulfone (**1a**) (mp 90—91 °C (90—91 °C)), p-tolylazo phenyl sulfone (**1b**) (mp 82—83 °C), phenylazo phenyl sulfone (**1c**) (mp 75—76 °C (76—77 °C)), p-tolylazo p-tolyl sulfone (**1d**) (mp 96—97 °C (96—97 °C)), and p-methoxyphenylazo p-methoxyphenyl sulfone (**1e**) (mp 111—112 °C) were prepared by the published procedures.[9]

General Procedure for the Reaction of Arylazo Aryl Sulfone with Carbon Monoxide Catalyzed by Tetrakis(triphenylphosphine)palladium(0). To a stirred solution containing arylazo aryl sulfone (2.0 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.2 mmol) in 10.0 cm^3 of benzene-acetic acid (1 : 1) at 80 °C, carbon monoxide was introduced by bubbling for 2 h. The crude reaction mixture was then concentrated and chromatographed on silica gel, using ethyl acetate as the eluent. The products were identified by comparing their retention times of GC and the IR, ^{1}H NMR, and mass spectra with those of authentic samples.

General Procedure for the Reaction of Arylazo Aryl Sulfone with Carbon Monoxide and Nucleophiles Catalyzed by the Palladium(0) Complex. a) To a stirred solution containing arylazo aryl sulfone (2.0 mmol), nucleophile (alcohol or amine, 2.0 cm^3), and tetrakis(triphenylphosphine)palladium(0) (0.2 mmol) in 10.0 cm^3 of benzene at 80 °C, carbon monoxide was introduced by bubbling for 2 h. b) To a stirred suspension containing arylazo aryl sulfone (2.0 mmol), nucleophile (sodium methoxide or sodium acetate, 10.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.2 mmol) in 10.0 cm^3 of benzene at 80 °C, carbon monoxide was introduced by bubbling for 2 h. The crude reaction mixture was then concentrated and chromatographed on silica gel, using ethyl acetate as the eluent. The products were identified by comparing their retention times of GC and the IR, ^{1}H NMR, and mass spectra with those of authentic samples.

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