CHEMISTRY LETTERS, pp. 347-350, 1987.

Reaction of Arylazo Aryl Sulfone with Olefins in the Presence of Tetrakis(triphenylphosphine)palladium(0)

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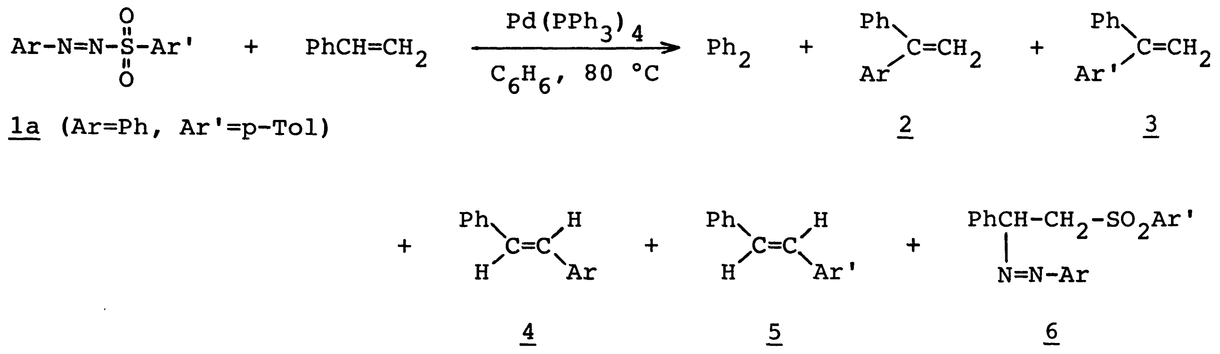
Catalytic reaction of arylazo aryl sulfone with olefins in the presence of tetrakis(triphenylphosphine)palladium(0) was investigated. Arylation of olefins was the major product, and 1:1 adduct of arylazo and arenesulfonyl group to olefins was obtained as minor product. Diarylpalladium(II) species was proposed as an intermediate in this reaction.

Recently, we have reported that arylazo aryl sulfones (1) are versatile precursors for aryl radicals, aryl cations, aryl anions, carbenes, and benzynes.1) The compound 1 is known to cleave homolytically under neutral or a little basic conditions both thermally and photochemically, and the resulting aryl radical works as an initiator of radical polymerization of olefins2) or arylates aromatic compounds.3) Recently, Kikukawa and Matsuda have reported that arenediazonium salt of N-nitroso-N-arylacetamides in the presence of palladium complex catalyst arylates olefins to afford arylolefins.4) This prompts us to investigate the reaction of arylazo aryl sulfone with olefins in the presence of palladium(0) catalyst, and the results will be described in this communication.5)

In a typical example, to a stirred solution containing 1.046 g (10 mmol) of styrene and 29 mg (0.01 mmol) of tetrakis(triphenylphosphine)palladium(0) in 2 cm^3 of benzene under nitrogen was added dropwise 523 mg (2 mmol) of phenylazo p-tolyl sulfone (1a) in 8 cm^3 of benzene over a period of 20 min at 80 °C, and the mixture was stirred for 2 h. TLC analysis showed that the products are separated in roughly two spots. These components were separated by column chromatography on silica-gel using hexane-ether mixture as an eluent. The former fraction was analyzed by GC (SE 30, 2 m) and identified by comparing their spectroscopic data with those authentic samples. The products were biphenyl 1%, 1,1-diphenylethylene (2) 10%, 1-phenyl-1-(p-tolyl)ethylene (3) 10%, (E)-stilbene (4) 32%, and (E)-1-phenyl-2-(p-tolyl)ethylene (5) 32%. Biphenyl seems to be formed by the thermal cleavage (non catalytic reaction) of 1a giving phenyl radical which reacted homolytically with solvent benzene. The products 2-5 seem to be formed by the catalytic reaction of 1a with palladium(0). It is interesting to note that both phenyl and p-tolyl groups of 1a arylated at α- and β-position of styrene in almost equal amount to give 2 or 3, and 4 or 5, respectively. The latter fraction was recrystallized from ethanol to give 155 mg of pale-yellow crystals which was determined as 2-phenyl-2-phenylazoethyl p-tolyl sulfone (6a) (yield 21%) on the basis of its spectral data comparing with authentic sample prepared by the method described in footnote.[6)] The adduct 6a has not been observed in the thermal or photochemical reaction of 1a with olefins. Therefore, 6a is considered to be the palladium(0) catalyzed reaction product with styrene.



1a (Ar=Ph, Ar'=p-Tol)

2 3

PhCH-CH$_2$-SO$_2$Ar' with N=N-Ar on the benzylic carbon

4 5 6

Similarly, the reaction of p-tolylazo phenyl sulfone (1b), phenylazo phenyl sulfone (1c), and p-tolylazo p-tolyl sulfone (1d) with styrene were carried out in the presence of tetrakis(triphenylphosphine)palladium(0) in benzene solution under nitrogen at 80 °C. The results are summarized in Table 1. It is of interest that product ratio 2:3 and 4:5 were almost the same both in the reactions of 1a and 1b, respectively. This suggests that a common reactive intermediate is formed from either 1a and 1b by the palladium(0) catalyzed reaction. When the Ar and Ar' groups of the azosulfone 1 are the same (as is the case of 1c and 1d), the products have became simplified.

Table 1. Reaction of Arylazo Aryl Sulfones with Styrene Catalyzed by Tetrakis(triphenylphosphine)palladium(0) in Benzene at 80 °C[a)]

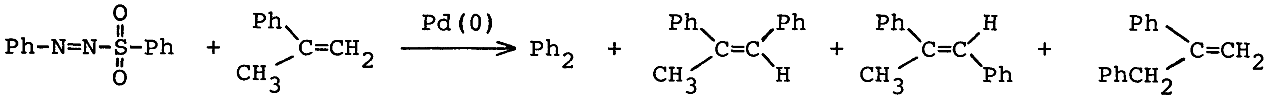
	Ar and Ar' in 1		Product, Yield/%					
	Ar	Ar'	ArC_6H_5	2	3	4	5	6
1a	C_6H_5	$p\text{-}CH_3C_6H_4$	1	10	10	32	32	21
1b	$p\text{-}CH_3C_6H_4$	C_6H_5	1	11	12	33	32	22
1c	C_6H_5	C_6H_5	2	17		56		32
1d	$p\text{-}CH_3C_6H_4$	$p\text{-}CH_3C_6H_4$	2	15		49		35

a) The yields are based on the arylazo aryl sulfone used.

These reactions may be considered to proceed via oxidative addition of arylazo arylsulfone to palladium(0) catalyst giving Ar-N=N-Pd(II)-SO_2Ar' which adds to olefin, followed reductive elimination to afford product 6 regenerating Pd(0). The complex Ar-N=N-Pd(II)-SO_2Ar' splits off nitrogen and sulfur dioxide to form diarylpalladium(II) complex, Ar-Pd(II)-Ar', followed by addition with olefin and reductive elimination to give arylated olefins, arene, and Pd(0). Thus as a whole, a catalytic cycle may be achieved. The formation of diarylpalladium(II) species was supported by the detection of p,p'-dimethylbiphenyl in the palladium(0) catalyzed reaction of p-tolylazo p-tolyl sulfone in benzene. The formation of p,p'-dimethylbiphenyl is accounted for by the reductive elimination of di-p-tolylpalladium, p-Tol-Pd(II)-Tol-p, accompanied by regeneration of Pd(0). The formation of arene by the reductive elimination is difficult to detect when aryl group of 1 is phenyl. Then, the reaction of p-methoxyphenylazo p-tolyl sulfone with styrene in the presence of the palladium(0) catalyst was carried out in benzene and the formation of anisole and toluene was detected by GC-MS.

Reaction of phenylazo phenyl sulfone (1c) with 2-phenylpropene in the presence of the palladium(0) catalyst in benzene was also carried out in a similar conditions. The reaction products were determined as biphenyl 3%, (Z)-1,2-diphenylpropene (7) 12%, (E)-1,2-diphenylpropene (8) 30%, and 2,3-diphenylpropene (9) 35%.

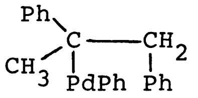
The formation of 9 is of interest since it provides us good mechanistic suggestion involving diphenylpalladium(II) species. The intermediate will add to 2-phenylpropene giving the adduct 10. The PhPd group in 10 can be eliminated with



1c 7 8 9

either β-hydrogen of methyl or methylene group of 10 to give 9 and 7 or 8, respectively.

The reaction did not be catalyzed by a palladium(II) acetate or tris(dibenzylidene)dipalladium(0). Further studies on the scope and limitation of these reactions are now in progress.



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5) There is no report on the arylation of olefins with 1. The reaction has a characteristic feature that both of the aryl groups of 1 can be introduced into olefins.
6) 2-Phenyl-2-phenylazoethyl p-tolyl sulfone (6a) was prepared by refluxing a solution containing 2.0 g of phenacyl bromide and 2.5 g of sodium p-toluenesulfinate in 40 cm^3 of methanol afforded 1.4 g of colorless crystals of phenacyl p-tolyl sulfone (mp 97-98 °C from ethanol), which was treated with 0.53 g of phenylhydrazine and a catalytic amount of p-toluenesulfonic acid in 20 cm^3 of methanol at reflux for 2 h: mp (dec.) 139-140 °C; IR (KBr) 1160 and 1310 cm^{-1}; ^{1}H NMR (CDCl$_3$) $\delta = 2.25$ (3H, s), 3.5-3.9 (1H, m), 4.2-4.6 (1H, m), 5.3-5.6 (1H, m), 7.15 (2H, d, $J = 8.4$ Hz), 7.25 (5H, s), 7.64 (2H, d, $J = 8.4$ Hz), 7.2-7.4 (5H, m); MS, m/z 354 (M$^+$), 285 (M$^+$-Ph), 209 (M$^+$-CH$_3$C$_6$H$_4$SO$_2$).

(Received October 25, 1986)