

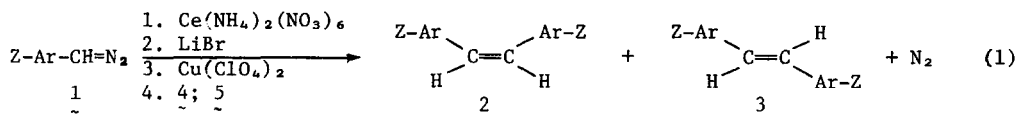
RHODIUM ION CATALYZED DECOMPOSITION OF ARYLDIAZOALKANES

B. K. Ravi Shankar and Harold Shechter\*

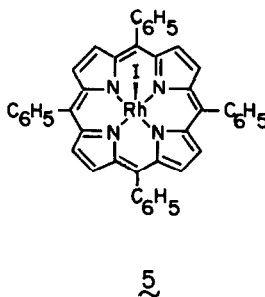
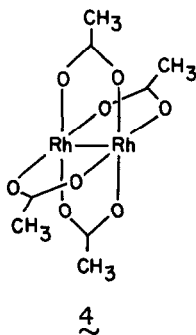
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Abstract: Aryldiazomethanes are converted by rhodium(II) acetate and iodorrhodium(III) tetraphenylporphyrin to cis- rather than trans-1,2-diarylethylenes. Secondary aryldiazoalkanes react with rhodium(II) acetate to give azines.

Decompositions of primary aryldiazomethanes (1) by ceric ammonium nitrate,<sup>1a</sup> lithium bromide,<sup>1b</sup> or copper(II) salts (perchlorate and bromide)<sup>1c</sup> occur with loss of nitrogen to give cis-1,2-diarylethylenes (2) in preference to their trans-isomers (3). Although these reactions are of mechanistic interest,<sup>1</sup> they have not been developed as general methods. The behavior of



aryldiazoalkanes<sup>2a</sup> with rhodium(II) acetate (4, Rh<sub>2</sub>(OAc)<sub>4</sub>)<sup>2b</sup> and iodorrhodium(III) tetraphenylporphyrin (5)<sup>2c</sup> is now reported.<sup>2d</sup> The results of note are: (1) reactions of varied aryldiazomethanes (1) and 4 to give 2 rather than 3 are rapid, efficient and highly selective,<sup>3a-c</sup> (2) the specificities in the conversions of 1 by 5 to 2 are advantageous,<sup>3b-c</sup> and (3) secondary aryldiazoalkanes react with 4 to form azines essentially exclusively.



In the present experiments with 1 and 4, the decompositions were usually effected by adding the catalyst (~10 mg) to 1 (~2 mmol) in tetrahydrofuran (20 ml) at ~-20°C and warming the mixtures. At -0°C the red solutions evolve nitrogen rapidly (<10 min) and turn green. The product mixtures of 2 and 3 are isolated upon concentration of the solutions and column chromatography. Table 1 summarizes the yields and the ratios of 2 and 3 obtained. Increasing the molar proportions of 1 to 4 to as high as 160:1 does not alter the percentages of 2 and 3. The products were assigned upon comparing their IR and NMR spectra with literature values and that of authentic samples. The mixtures of 2 and 3 were analyzed by LC comparisons with pure 3 as prepared by

isomerizations of the products with iodine and then column chromatography.

Table 1

Conversion of Aryldiazomethanes (1) to Cis (2) and Trans (3)-1,2-Diarylethylenes by Rhodium(II) Acetate (4) and by Iodorhodium(III) Tetraphenylporphyrin (5).

Aryldiazomethanes ( <u>1</u> )	Ethylenes <u>2</u> and <u>3</u>	Yield <sup>a</sup>		Ratio <sup>a</sup>		Yield <sup>b</sup>		Ratio <sup>b</sup>	
		(%)	<u>2</u> / <u>3</u>	(%)	<u>2</u> / <u>3</u>	(%)	<u>2</u> / <u>3</u>		
PhCHN <sub>2</sub>	PhCH=CHPh	84	4.0	67	7.33				
p-CH <sub>3</sub> -PhCHN <sub>2</sub>	p-CH <sub>3</sub> -PhCH=CHPh-CH <sub>3</sub> -p	77	3.8	55	12.6				
p-CH <sub>3</sub> O-PhCHN <sub>2</sub>	p-CH <sub>3</sub> O-PhCH=CHPh-OCH <sub>3</sub> -p	61	>2.5 <sup>c</sup>						
p-Cl-PhCHN <sub>2</sub>	p-Cl-PhCH=CHPh-Cl-p	87	4.3	57	8.8				
p-O <sub>2</sub> N-PhCHN <sub>2</sub>	p-O <sub>2</sub> N-PhCH=CHPh-NO <sub>2</sub> -p	70	>4.6 <sup>c</sup>						
o-CH <sub>3</sub> -PhCHN <sub>2</sub>	o-CH <sub>3</sub> -PhCH=CHPh-CH <sub>3</sub> -o	88	11.9						
o-CH <sub>3</sub> O-PhCHN <sub>2</sub>	o-CH <sub>3</sub> O-PhCH=CHPh-OCH <sub>3</sub> -o	94	3.5						
o-Cl-PhCHN <sub>2</sub>	o-Cl-PhCH=CHPh-Cl-o	99	7.2						
m-CH <sub>3</sub> -PhCHN <sub>2</sub>	m-CH <sub>3</sub> -PhCH=CHPh-CH <sub>3</sub> -m	74	4.5						
1-Naphthyl-CHN <sub>2</sub>	1-Naphthyl-CH=CH-1-naphthyl	91	11.5						
2-Naphthyl-CHN <sub>2</sub>	2-Naphthyl-CH=CH-2-naphthyl	83	3.3 <sup>d</sup>						
9-Phenanthryl-CHN <sub>2</sub>	9-Phenanthryl-CH=CH-9-phenanthryl	85	9.7						
2-Thienyl-CHN <sub>2</sub>	2-Thienyl-CH=CH-2-thienyl	>38	2.7						
2,4,6-(CH <sub>3</sub> ) <sub>3</sub> -PhCHN <sub>2</sub>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> -PhCH=CHPh-(CH <sub>3</sub> ) <sub>3</sub> -2,4,6	90	0.66 <sup>d</sup>	20	24.4				

<sup>a</sup>From 1 and 4. <sup>b</sup>From 1 and 5. <sup>c</sup>The exact ratios could not be determined accurately because of the insolubilities of 3. <sup>d</sup>The ethylenes were separated preparatively in the stated yields and ratios by column chromatography on silica gel using hexane/benzene as eluent.

The study reveals (Table 1) that (1) ortho, meta and para-substituted phenyldiazomethanes, 1- and 2-naphthyldiazomethanes, 9-phenanthryldiazomethane and 2-thienyldiazomethane are converted effectively to cis-(2) rather than trans-(3)-1,2-diarylethylenes, (2) electron-donating or electron-withdrawing para-substituents do not greatly alter the conversions of phenyldiazomethanes to cis- rather than trans-stilbenes, (3) the presence of ortho-substituents of varied structural and electronic types in 1 leads to significantly enhanced conversions to 2 over 3 and to increased overall yields of ethylenes and (4) the catalyst, 4, does not isomerize 2 or 3 after their formation. Of further interest is that 2,4,6-trimethylphenyldiazomethane, a highly encumbered reactant, does give trans- rather than cis-2,4,6,2',4',6'-hexamethylstilbenes; however, the ratio of the trans- to cis-ethylene is only 1:0.66.

The behavior of 4 with secondary aryldiazoalkanes (6) is different than for 1 in that azines (7; Eq. 2, Table 2) are produced; tetrasubstituted ethylenes (8-9, Eq. 3) are not formed. Efforts to convert 6 to 8 and 9 by direct or inverse addition of 4 to 6 in tetrahydrofuran or benzene at 0 to 78°C or by varying the ratios of 6 to catalyst all failed. Decomposition of a mixture of phenyldiazomethane and 1-diazo-1-phenylethane with 4 does give some 1,2-diphenyl-1-propenes along with cis- and trans-stilbenes and azines. The method, however, is not promising for efficient preparation of trisubstituted ethylenes.

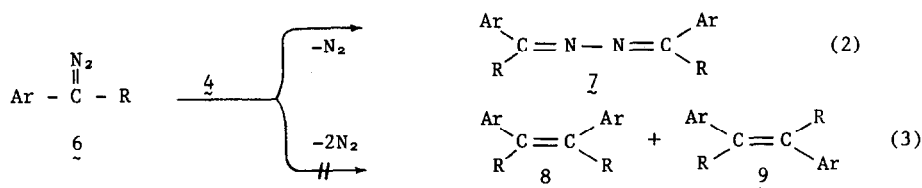


Table 2

Conversion of Secondary Aryldiazoalkanes (6) to Azines (7) by Rhodium(II) Acetate (4).

<u>Aryldiazoalkanes</u> (6)	<u>Azine</u> (7)	<u>Yield</u> (%)
PhC(N <sub>2</sub> )CH <sub>3</sub>	Acetophenone	69
p-CH <sub>3</sub> -PhC(N <sub>2</sub> )CH <sub>3</sub>	p-Methylacetophenone	80
p-CH <sub>3</sub> O-PhC(N <sub>2</sub> )CH <sub>3</sub>	p-Methoxyacetophenone	83
p-Cl-PhC(N <sub>2</sub> )CH <sub>3</sub>	p-Chloroacetophenone	85
p-NC-PhC(N <sub>2</sub> )CH <sub>3</sub>	p-Cyanoacetophenone	69
PhC(N <sub>2</sub> )Ph	Benzophenone	62
2-Naphthyl-C(N <sub>2</sub> )CH <sub>3</sub>	2-Acetonaphthenone	60

The reactions of 1 with 5, a rhodium(III) catalyst with a ligand of enormous bulk, were then investigated. The overall yields of 2 and 3 upon use of 5 (Table 1) are somewhat lower when compared to 4. Of importance, however, is the increase in the cis/trans selectivities in formation of 2 and 3. Table 1 also reveals that (1) the electrical nature of a substituent in 1 has only a minor effect on the cis/trans selectivities whereas (2) steric effects play a major role on stereoselectivity as evidenced by the preferential formation (24.4:1) of cis- rather than trans-2,4,6,2',4',6'-hexamethylstilbenes. Thus, decomposition of 1 by catalyst 4 offers a seeming advantageous entry to very hindered ethylenes (2).

Catalysis in reactions of 1 and 4 may involve rhodium ylides (10) as in Eq. 4.<sup>4</sup> Conversions of 1 to 2 rather than 3 can be rationalized by (1) addition of 1 to 10 as controlled by conformer steric effects as augmented by attraction of the diazonium and the rhodium moieties, (2) rotation of 11 and 12 and (3) trans-elimination of nitrogen and the catalyst (4). Thus 11 would be formed in preference to 12 and convert to 2 via 13. Such mechanisms are similar to those proposed for copper (II)-catalyzed conversions of 1 to 2 and 3<sup>1c</sup> and, on the basis of steric effects, rationalize the increased cis/trans ratios of 2:3 from reactions of 4 with ortho-substituted phenyldiazomethanes and from 1 and 5. Reactions of secondary ylides such as 15 (Eq. 5) possibly occur on nitrogen rather than carbon of 6 because of steric and electrical effects and thus yield 7 instead of 8 and 9.

