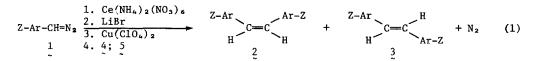
RHODIUM ION CATALYZED DECOMPOSITION OF ARYLDIAZOALKANES

B. K. Ravi Shankar and Harold Shechter*

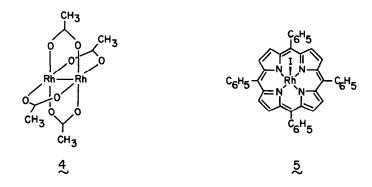
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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

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



aryldiazoalkanes^{2a} with rhodium(II) acetate $(4, Rh_2(OAc)_4)^{2b}$ and iodorhodium(III) tetraphenylporphyrin $(5)^{2c}$ is now reported.^{2d} 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, ^{3a-c} (2) the specificities in the conversions of 1 by 5 to 2 are advantageous, ^{3b-c} 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 l

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

Aryldiazomethanes (1)	Ethylenes 2 and 3	<u>Yield</u> ^a	<u>Ratio</u> a	<u>Yield</u> ^b	<u>Ratio</u> b
		(%)	2/3	(%)	2/3
PhCHN ₂	PhCH=CHPh	84	4.0	67	7.33
<u>p</u> -CH ₃ -PhCHN ₂	\underline{p} -CH ₃ -PhCH=CHPh-CH ₃ - \underline{p}	77	3.8	55	12.6
p-CH ₃ O-PhCHN ₂	<u>p</u> -CH ₃ O-PhCH=CHPh-OCH ₃ - <u>p</u>	61	>2.5 ^c		
p-Cl-PhCHN ₂	<u>p</u> -C1-PhCH=CHPh-C1- <u>p</u>	87	4.3	57	8.8
p-02N-PhCHN2	p-02N-PhCH=CHPh-NO2-p	70	>4.6 ^C		
o-CH ₃ -PhCHN ₂	o-CH ₃ -PhCH=CHPh-CH ₃ -o	88	11.9		
o-CH ₃ O-PhCHN ₂	<u>o</u> −CH₃O−PhCH=CHPh−OCH₃− <u>o</u>	94	3.5		
o-C1-PhCHN ₂	o-Cl-PhCH=CHPh-Cl-o	99	7.2		
m-CH ₃ -PhCHN ₂	\underline{m} -CH ₃ -PhCH=CHPh-CH ₃ - \underline{m}	74	4.5		
l-Naphthyl-CHN ₂	1-Naphthy1-CH=CH-1-naphthy1	91	11.5		
2-Naphthy1-CHN ₂	2-Naphthy1-CH=CH-2-naphthy1	83	3.3 ^d		
9-Phenanthry1-CHN ₂	9-Phenanthry1-CH=CH-9-phenanthry1	85	9.7		
2-Thieny1-CHN ₂	2-Thieny1-CH=CH-2-thieny1	>38	2.7		
2,4,6-(CH ₃) ₃ -PhCHN ₂	$2,4,6-(CH_3)_3-PhCH=CHPh-(CH_3)_3-2,4,6$	90	0.66 ^d	20	24.4

^aFrom 1 and 4. ^bFrom 1 and 5. ^cThe exact ratios could not be determined accurately because of the insolubilities of $\tilde{3}$. ^dThe 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) <u>ortho, meta</u> and <u>para</u>-substituted phenyldiazomethanes, 1- and 2-naphthyldiazomethanes, 9-phenanthryldiazomethane and 2-thienyldiazomethane are converted effectively to <u>cis</u>-(2) rather than <u>trans</u>-(3)-1,2-diarylethylenes, (2) electron-donating or electron-withdrawing <u>para</u>-substituents do not greatly alter the conversions of phenyldiazomethanes to <u>cis</u>- rather than <u>trans</u>-stilbenes, (3) the presence of <u>ortho</u>-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 <u>trans</u>- rather than <u>cis</u>-2,4,6,2',4',6'-hexamethylstilbenes; however, the ratio of the <u>trans</u>- to <u>cis</u>-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-1propenes along with <u>cis</u>- and <u>trans</u>-stilbenes and azines. The method, however, is not promising for efficient preparation of trisubstituted ethylenes.

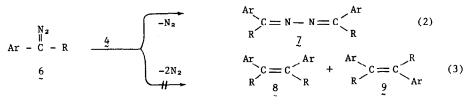


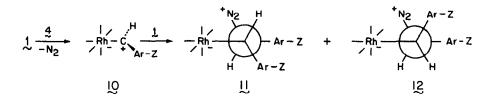
Table 2

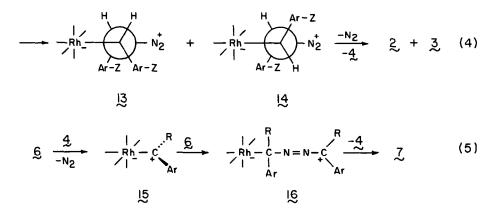
Conversion of Secondary Aryldiazoalkanes (6) to Azines (7) by Rhodium(II) Acetate (4).

Azine (7)	Yield
	(%)
Acetophenone	69
<u>p-</u> Methylacetophenone	80
p-Methoxyacetophenone	83
<u>p</u> -Chloroacetophenone	85
p-Cyanoacetophenone	69
Benzophenone	62
2-Acetonaphthenone	60
	Acetophenone p-Methylacetophenone p-Methoxyacetophenone p-Chloroacetophenone p-Cyanoacetophenone Benzophenone

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 <u>cis/trans</u> 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 <u>cis/trans</u> selectivities whereas (2) steric effects play a major role on stereoselectivity as evidenced by the preferential formation (24.4:1) of <u>cis</u>- rather than <u>trans</u>-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. 4.⁴ 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^{1c} and, on the basis of steric effects, rationalize the increased <u>cis/trans</u> ratios of 2:3 from reactions of 4 with ortho-substituted phenyldiazomethanes and from 1 and 5. Reactions of steric and electrical effects and thus yield 7 instead of 8 and 9.





Acknowledgment. This research was supported by the National Science Foundation.

REFERENCES

- (a) W. S. Trahanovsky, M. D. Robins and D. Smick, J. Am. Chem. Soc., 93, 2086 (1971). (b) M. Nakajima and J. P. Anselme, <u>Chem. Comm.</u>, 796 (1980). (c) T. Oshina and T. Nagai, <u>Tetrahedron Lett.</u>, 21, 1251 (1980).
- (a) Diazoalkanes 1 and 6 were obtained from arylsulfonylhydrazones in tetramethylguanidine at 50-60°C upon cooling the mixtures, adding ether, aqueous extraction and concentrating the ether extracts. (b) R. Legzdins, R. W. Mitchell, G. L. Rampal, J. D. Ruddick and G. Wilkinson, J. Chem. Soc., (A), 3322 (1970). (c) H. J. Callot and C. Piechocki, <u>Tetrahedron Lett.</u>, 21, 3489 (1980). (d) A. J. Hubert, A. F. Noels, A. J. Anciaux and P. Teyssie, <u>Synthesis</u>, 9, 600 (1976), report that in reactions of ethyl diazoacetate, rhodium(II) carboxylates and olefins to give cyclopropanes, diethyl maleate and diethyl fumarate are formed.
- 3. (a) Phenyldiazomethane and its p-methyl and p-chloro derivatives react with ceric ammonium nitrate (CAN) at -5°C to give the corresponding stilbenes (2 and 3) in 80-98% yields in 5.5:1, 3.2:1 and 2.3:1 ratios, respectively. However, CAN öxidizës p-nitro- and α-tri-fluoromethylphenyldiazomethanes and converts p-methoxy-, o-chloro- and p-methylphenyldiazomethanes and 1- and 2-naphthyldiazomethanes to complex products.^{1a} (b) Reactions of copper perchlorate and copper bromide with phenyl, p-tolyl- and p-chlorophenyldiazomethanes at 0-40°C for 1-4 hr give 2 and 3, respectively, in 1.4-2.5:1 ratios in 74-92% yields.^{1b} The copper catalysts are thus less stereoselective than 4. (c) Phenyldiazomethane is converted (48-76%, 6-7 days) by lithium bromide (0.5-1.0 equiv) in ether at room temperature to cisstilbene in 76-90% yields containing trace amounts of trans-stilbene.^{1C} Much larger ratios of lithium bromide (4 equiv) are necessary to decompose p-methoxyphenyldiazomethane (in 4 days) to cis- and trans-p,p'-dimethoxystilbenes in 64 and 4% yields, respectively. Further, p-chlorophenyldiazomethane is converted by lithium bromide (1 equiv) in 11 days to cis- and trans-p,p'-dichlorostilbenes in 61 and 15% yields.
- 4. (a) Study of other Rh(II and III) catalysts is in progress. (b) Bridged dirhodium tetraace-toxy moleties are assumed in 10-16. (c) Electron-transfer to give radical-cation intermediates^{1a} is not a general mechanism for both 4 and 5 because the ratios of 2:3 are catalyst dependent. (d) An alternate interpretation for formation of 2 over 3 is that (l) addition of 10 to 1 is sterically controlled in which (a) the aryl groups and (b) the rhodium ylide and the diazonium ion moleties, respectively, are preferentially trans and (2) reaction is completed upon rotation within the conformer adducts because of attraction of the diazonium and the rhodium moleties and then cis-elimination of nitrogen and the catalyst. (e) Reactions of 1 and 6 with 4 with unbridging of the acetoxy groups to form dirhodiumcyclopropane intermediates^{4f²h} which react with 1 and 6 are to be considered in subsequent publications. (f) W. A. Herrmann, K. Kruger, R. Goddard and I. Bernal, J. Organometal. Chem., 140, 73 (1977). (g) N. M. Boag, M. Green, R. M. Mills, G. Y. Pain, F. G. A. Stone and P. Woodward, Chem. Comm., 1971 (1980). (h) B. K. Ravi Shankar, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1981.

(Received in USA 31 December 1981)