

FORMATION AND REACTIONS OF ARYLDIAZOMETHANE RADICAL CATIONS

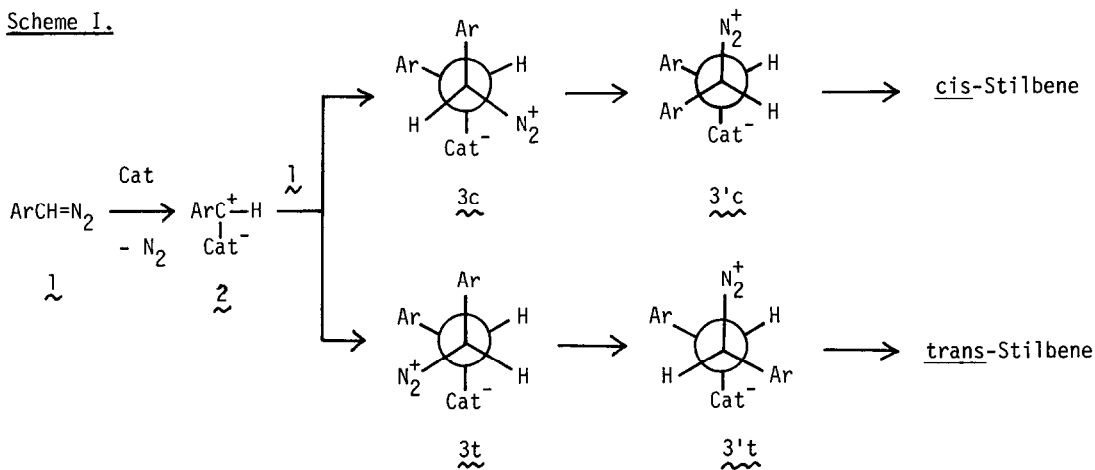
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Dicyanoanthracene-sensitized photolysis of aryldiazomethanes affords stilbenes with *cis/trans* ratios of ~3 via free radical cations; anodic oxidation gives similar results but via radical cations adsorbed on electrode surface.

Dimerizations of diazo compounds to afford olefins are well known as carbenoid reactions catalyzed by transition metals such as copper salts.¹⁾ Of interest are catalytic decompositions of aryldiazomethanes to yield *cis*-stilbenes in preference to more stable *trans*-isomers, e.g., ceric ammonium nitrate,²⁾ cupric salts,³⁾ lithium bromide,⁴⁾ and rhodium catalysts.⁵⁾ One explanation for the predominant formation of *cis*-stilbene is based on two assumptions that adduct 3_c , involving an electrostatic attraction between diazonium and catalyst moiety, is sterically more stable than 3_t and that stilbenes are formed from $3'$ by *trans*-elimination of nitrogen and the catalyst (Scheme I).^{3,5)}

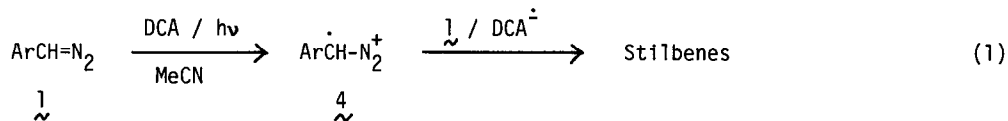
Scheme I.



However, it is not certain whether the electrostatic attraction in 3 is important and the elimination is *trans* or *cis*. Herein, we wish to report that *cis*-stilbenes are also obtained predominantly by the one-electron oxidation of aryldiazomethanes via their radical cations according to a pathway different from Scheme I.

In the course of studies on the sensitized reaction of diazo compounds with oxygen,⁶⁾ we were interested in the formation and reactivity of diazo radical cations. One-electron oxi-

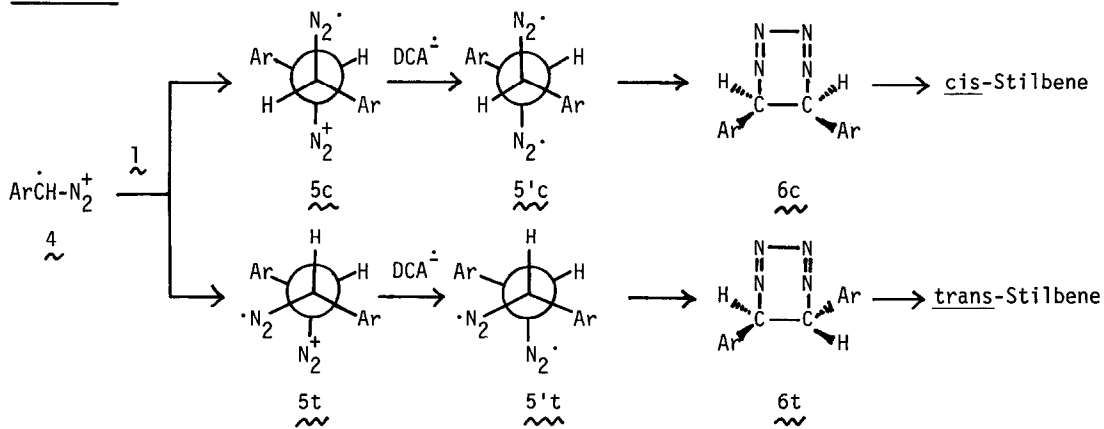
ditions of diazo compounds are not clarified although some studies have been reported on anodic,⁷⁾ Ce(IV),²⁾ and amine radical cation oxidations.⁸⁾ When aryldiazomethanes (1) were photolyzed in the presence of 9,10-dicyanoanthracene (DCA), cis-stilbenes were obtained predominantly. Thus, DCA-sensitized photolysis of 3-10 mM phenyldiazomethane (1a) in acetonitrile under argon afforded cis- and trans-stilbenes in over 95% yields, cis/trans ratio being 3.1. Similar results were obtained for other aryldiazomethanes (Table 1). In contrast, the direct photolysis of 1 in the absence of DCA resulted in much lower yields of stilbenes and lower cis/trans ratios of ~ 1 . A direct photolysis of 1a in MeOH-MeCN (1:9) yielded benzylmethyl ether as an O-H insertion product of phenylcarbene, while the DCA-sensitized reaction in the same solvent afforded high yields of stilbenes (Table 2). These facts clearly suggest that stilbenes by the DCA sensitization are formed via an intermediates other than free carbenes. Since DCA is known as an efficient sensitizer to effect one-electron oxidations,⁹⁾ the stilbenes are probably formed via aryldiazomethane radical cations (4) (eq. 1).



The sensitized photolysis under oxygen atmosphere afforded solely benzaldehydes, suggesting effective trapping of 4 with O_2 .¹⁰⁾ When the DCA-sensitized photolysis of 1a was conducted in benzene, 7-phenylcycloheptatriene, a product of carbene reaction, was obtained as a major product, indicating an energy transfer from DCA^* to 1a in non-polar solvent rather than electron transfer.

All of the above results suggest that the DCA-sensitized reaction in MeCN produces radical cation 4 (eq. 1) and the predominant formation of cis-stilbenes seems to be reasonably explained by a mechanism as outlined in Scheme II.

Scheme II.



The addition of radical cations 4 to 1 should be very fast since trapping by olefins was not effective. Apparently, the adduct 5c is sterically much stable than 5t; 5 affords biradical 5' by electron transfer from $\text{DCA}^{\cdot-}$.¹¹⁾ Stilbenes are presumably formed via cis-elimination of

Table 1. Photolysis of Phenylidiazomethanes in MeCN^{a)}

ArCH=N ₂	Conditions Sens/hv	Conversion (%)	Stilbene (%)		cis trans
			cis	trans	
A) DCA-Sensitized Photolysis					
<u>1a</u> PhCH=N ₂	DCA/1.5 h	100	74	24	3.1
<u>1b</u> p-MeC ₆ H ₄ CH=N ₂	DCA/5 h	70	63	19	3.3
<u>1c</u> p-MeOC ₆ H ₄ CH=N ₂	DCA/5 h	53	53	17	3.1
<u>1d</u> p-ClC ₆ H ₄ CH=N ₂	DCA/1.5 h	100	70	24	2.9
B) Direct Photolysis					
<u>1a</u> PhCH=N ₂	none/15 h	99	4	5	0.8
<u>1c</u> p-MeOC ₆ H ₄ CH=N ₂	none/15 h	62	15	13	1.2
<u>1d</u> p-ClC ₆ H ₄ CH=N ₂	none/20 h	94	3	4	0.8

a) Irradiation of 3-4 mM phenylidiazomethanes at >400 nm in MeCN at 20°C under argon. As a sensitizer 0.4 mM DCA was added and stilbenes were not isomerized under the photolysis conditions.

Table 2. Photolysis of Phenylidiazomethane (1a) under Various Conditions^{a)}

Conditions Sens/additive/hv	Conversion (%)	Stilbene (%)			Others
		cis	trans	(cis/trans)	
DCA / 1.5 h	100	74	24	(3.1)	
DCA / 10% MeOH/ 1.5 h	100	60	18	(3.3)	PhCH ₂ OMe (5%)
none / 10% MeOH/ 16 h	98	2	3	(0.7)	PhCH ₂ OMe (87%)
DCA / 10% C ₆ H ₁₂ / 15 h	100	78	19	(4.1)	PhCH ₂ C ₆ H ₁₁ (0.5%)
DCA / O ₂ / 15 min	100	0	0		PhCHO (95%)

a) Irradiation of 3-4 mM 1 and 0.4 mM DCA at >400 nm in MeCN; additive % means vol.%.

nitrogen from unstable¹²⁾ tetrazine 6c or 6t. According to Scheme II, the predominant formation of cis-stilbene is well understood on the basis of relative stabilities of adducts 5c and 5t.

When 1a was oxidized anodically with Pt electrode in MeCN (+ 1.2 V vs. Ag/AgCl; 0.1 M LiClO₄), stilbenes were obtained almost quantitatively, cis/trans ratio being 4.2. The electrolytic reaction proceeds via radical chain mechanism since the resulting current efficiency are 7.5 and 39 mol/F with 4.5 and 16 mM 1a. Interestingly, stilbenes were likewise produced even under oxygen; that is, radical cation 4 could not be trapped by O₂. Thus, the cation radical chain decomposition as reported by Pragst and Jugelt¹³⁾ should proceed by diazo compounds adsorbed on electrode surface. The electrolysis of diphenylidiazomethane afforded tetraphenylethylene in 80% yield, while the DCA-sensitized photolysis gave no olefin. Presumably, the C-C formation is facilitated by adsorption on electrode surface. But, the resulting cis/trans ratio of stilbene similar to the DCA-sensitized photolysis indicates that the olefins by electrolysis of 1 are produced via a pathway similar to Scheme II. Further studies on diazo-

methane radical cations are under way.

References and Notes

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- 10) Presumably, carbonyl oxide intermediates are involved in the oxygenation of PhCHO just as PhCHO and singlet oxygen yield PhCHO almost quantitatively.⁶⁾
- 11) The quantum yield (~ 0.05) for the DCA-sensitized photolysis does not increase with the concentration of PhCHO , suggesting a non-chain nature of the photolysis.
- 12) No tetrazine has been synthesized as yet; A. E. A. Porter, "Comprehensive Organic Chemistry", Vol. 4, P. S. Sannes, ed., Pergamon Press, Oxford, 1979, p 150.
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