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Diazomethane Radical Cations as a Dipolarophile in the Dimeric Olefin Formation from Diazo-compounds

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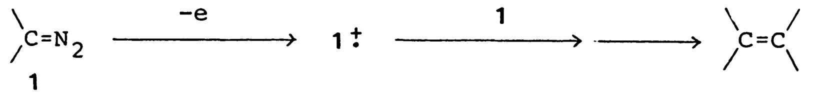
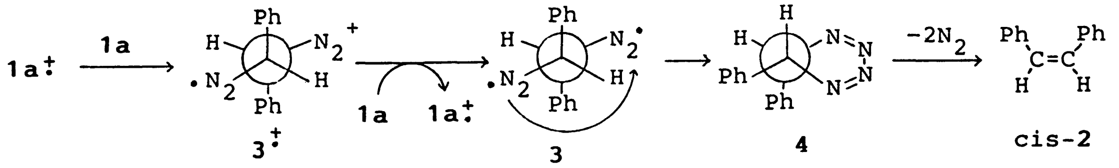
A novel cycloaddition mechanism involving diazomethane radical cations is proposed for the dimeric olefin formation by the one-electron oxidation of diazo-compounds. The preference of cis-stilbene formation from phenyldiazomethane is understood by a secondary orbital interaction of phenyl groups on the cycloaddition step.

Reactions involving electron-transfer are one of the most interesting fields in current chemistry. Diazomethanes have been reported to give dimeric olefins, in addition to the well-known metal-catalyzed decomposition,[1)] by one-electron oxidation.[2,3)]



(1)

However, the keypoint reaction of **1**$^{+\cdot}$ with **1** has not been clarified. As we noted earlier, mechanistically most interesting is the photosensitized oxidation or anodic oxidation of phenyldiazomethane (**1a**) to give cis-stilbene (cis-**2**) in preference to its more stable trans-isomer.[2)] Then we proposed tentatively a stepwise mechanism (Eq. 2) involving the addition of **1a**$^{+\cdot}$ to **1a** to yield a diazenyl radical (**3**), followed by its cyclization to a tetrazine (**4**).



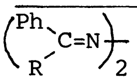
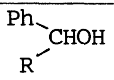
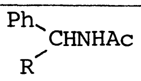
(2)

But the scheme became unlikely since it was recently established that aliphatic diazenyls are quite unstable and eliminate nitrogen much faster than their intramolecular radical recombination.[4)]

Diazo-compounds are known as a typical 1,3-dipolar species and have been shown to have C-N-N three-centered π-orbitals that are perpendicular to the molecular plane and are occupied by four electrons.[5)] Recently, we have reported on ESR spectra of aryldiazomethane radical cations generated by electrolysis in ESR cavity at low temperature, revealing their unique electronic structures.[6] Quite an interesting turnover takes place in the HOMO and LUMO on going from aryldiazomethanes to the corresponding radical cations. The latter has only two electrons on the three-centered π-orbitals and is therefore expected to behave as dienophiles or dipolarophiles in a manner similar to allyl cations.[7] Herein, we wish to report that, by the one-electron oxidation of aryldiazomethanes, dimeric olefins are formed via a novel cycloaddition of their radical cations as dipolarophiles.

One-electron oxidation of phenyldiazomethane (**1a**) with catalytic amounts of copper(II) perchlorate or tris(p-bromophenyl)aminium hexachloroantimonate in acetonitrile at room temperature afforded stilbene, the cis/trans ratio being 3-4, as in the case of photosensitized or anodic oxidation.[2] The oxidation of diphenyldiazomethane (**1b**) under similar conditions gave dimeric olefin in high yields.[3] Then we examined the oxidation of phenylmethyldiazomethane (**1c**) and phenylethyldiazomethane (**1d**), and found that the yields of dimeric olefins were quite low and a mixture of an azine, alcohol, and acetamide was obtained as coupling products of **1**$^{+\cdot}$ with **1**, water, and MeCN (Table 1). The sharp contrast is probably due to the significant steric hindrance of methyl and ethyl groups for the C-C coupling reaction. This may be supported by the following two observations. (i) The one-electron oxidation of 1:1 mixture of **1a** (R=H) and **1d** (R=Et) gave an almost statistical yield (37%) of cross-coupled olefin PhCH=C(Et)Ph, the cis/trans ratio being 2, in addition to stilbene (24%). This fact suggests that the steric hindrance for the coupling between **1d**$^{+\cdot}$ and **1d** is significantly reduced for the coupling between **1d**$^{+\cdot}$ and **1a** or **1a**$^{+\cdot}$ and **1d**.[8] (ii) A bisdiazo-compound **1e** was oxidized to give an olefin **5** in a good yield (84%); presumably the steric repulsion in this case is minimized because of the formation of an intramolecular six-

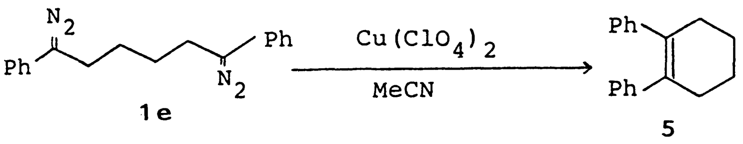
Table 1. Products on one-electron oxidation of $Ph(R)C=N_2$[a)]

Diazoalkane (R)	Oxidants (equiv.)	Ph(R)C=C(R)Ph (%)	(cis/trans)	Other products (%)			
				 $(Ph(R)C=N)_2$	 $Ph(R)CHOH$	 $Ph(R)CHNHAc$	others
1a (R=H)	Cu^{2+} (0.015)	97	(3.6)	<1	0	0	
	$Ar_3N^{+\cdot}$ (0.022)	98	(3.8)	<1	0	0	
	Electrolysis[b)]	97	(4.2)	<1	0	0	
1b (R=Rh)	Cu^{2+} (0.082)	76		5	0	0	
	$Ar_3N^{+\cdot}$ (0.12)	82		<1	0	0	
	Electrolysis[b)]	80		<1	0	0	
1c (R=Me)	Cu^{2+} (0.18)	4	(1.0)	6	26	10	$PhCH=CH_2$ (20)
1d (R=Et)	Cu^{2+} (0.42)	5	(1.5)	60	2	2	PhCH=CHMe (14)
	$Ar_3N^{+\cdot}$ (0.64)	4	(1.0)	22	5	3	PhCH=CHMe (12) Ph(Et)CHCl(34)
	Electrolysis[b)]	2	(1.0)	5	19	25	PhCH=CHMe (15)

[a)] Oxidation of 4-15 mM **1** in acetonitrile at 20 °C under argon. Yields were determined by GLC.; $Cu^{2+} = Cu(ClO_4)_2$; $Ar_3N^{+\cdot} = (p\text{-}BrC_6H_4)_3N^{+\cdot}SbCl_6^-$.

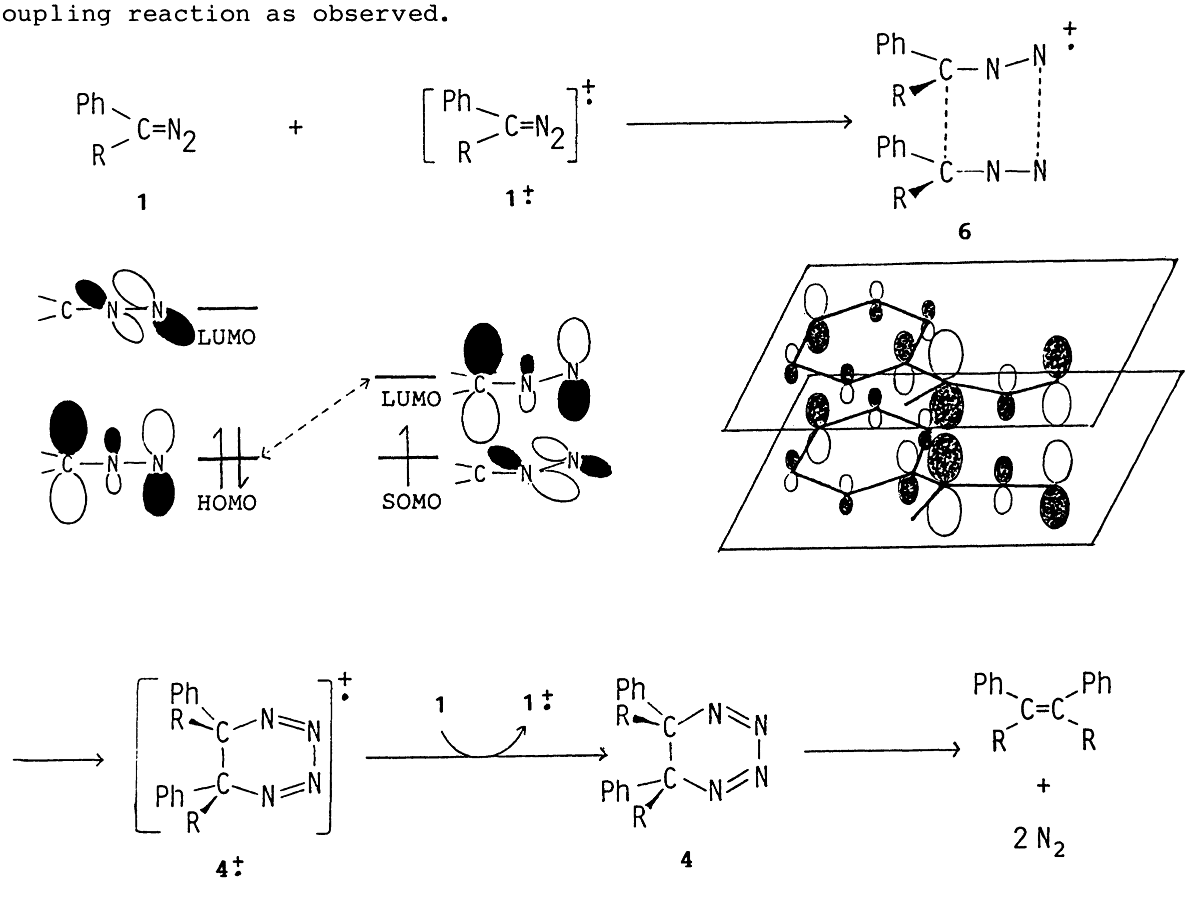
[b)] Anodic oxidation with Pt electrode (+1.2 V vs. Ag/AgCl; 0.1 M $LiClO_4$).

membered ring for the C-C coupling step. Thus, there are two features for the olefin-formation: the preference of cis-olefin formation from Ph(R)C=N_2 (**1**) and the significant steric effect of the α-alkyl group on the C-C coupling step.



(3)

We have shown from the ESR study on diazomethane radical cations (**1**$^{+\cdot}$)[6] that the HOMO of **1** is transformed into the LUMO of **1**$^{+\cdot}$ (see Scheme 1).[9] The frontier molecular orbital theory[10] tells that an ideal situation for orbital interaction between two molecules is achieved if interacting HOMO and LUMO are identical or close to each other in orbital energy. This situation may be realized in the present case between **1**-HOMO and **1**$^{+\cdot}$-LUMO, where a "face to face" interaction (**6**) is favored to achieve a $[_{\pi}4_s + {}_{\pi}2_s]$ cycloaddition as shown in Scheme 1.[11] The cyclized cation radical **4**$^{+\cdot}$ then abstracts one electron from **1** and eliminates two nitrogen molecules to afford olefins.[12] Since the overlap of the two phenyl groups is expected to stabilize the transition state **6** by a secondary orbital interaction as the known endo-selectivity for the Diels-Alder reactions, the predominant formation of cis-olefin may be well understood as shown in Scheme 1.[13,14] But for the case of **1c** (R=Me) and **1d** (R=Et), the energy of **6** would be significantly higher owing to the steric repulsion between the alkyl groups, reducing the C-C coupling reaction as observed.



Scheme 1.

Thus, it is shown that a turnover of electronic structures by one-electron removal from diazoalkane **1** may bring about a novel cycloaddition via its radical cation $\mathbf{1}^{\dagger}$.

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7) H. M. R. Hoffmann, Angew. Chem., Int. Ed. Engl., 23, 1 (1984).

8) E_p^{ox} of **1a** and **1d** are +0.94 V and +0.93 V (vs. Ag/AgCl in MeCN containing 0.1 M $LiClO_4$ at 100 mV/s), and hence the relative concentration of $\mathbf{1a}^{\dagger}$ and $\mathbf{1d}^{\dagger}$ are practically the same.

9) ESR spectra of $\mathbf{1b}^{\dagger}$ and $\mathbf{1c}^{\dagger}$ were previously reported,$^{6)}$ and those of $\mathbf{1a}^{\dagger}$ and $\mathbf{1d}^{\dagger}$ were found to be practically identical.

10) K. Fukui, "Molecular Orbital in Chemistry, Physics, and Biology," ed by P.-O. Löwdin and B. Pulmar, Academic Press, New York (1964), p. 513.

11) Interaction between another pair of frontier molecular orbitals (LUMO on **1** and SOMO on $\mathbf{1}^{\dagger}$) might play an important role on the cyclization as a back charge-transfer interaction.

12) 5,6-Dihydro-1,2,3,4-tetrazines such as **4** are quite unstable and have not been synthesized; A. E. A. Porter, "Comprehensive Organic Chemistry," ed by P. S. Sammes, Pergamon Press, Oxford (1979), Vol. 4, p. 150.

13) Decomposition of $\mathbf{4}^{\dagger}$ to olefin radical cation seems to be slower than the electron abstraction from **1** since cis-stilbene radical cation is known to be transformed to the more stable trans-isomer; F. D. Lewis, J. R. Petisce, J. D. Oxman, and M. J. Nepras, J. Am. Chem. Soc., 107, 203 (1985).

14) The preference for cis-stilbene formation has been also reported on the metal-catalyzed decomposition of **1a**. Since the cis/trans ratio of the product is affected by the bulkiness of metal ligands, the cis preference might be understood by the carbenoid mechanism; W. S. Trahanovsky, M. D. Robbins, and D. Smick, J. Am. Chem. Soc., 93, 2086 (1971); T. Oshima and T. Nagai, Tetrahedron Lett., 1979, 2789; T. Oshima and T. Nagai, Tetrahedron Lett., 1980, 1251; M. Nakajima and J.-P. Anselme, J. Chem. Soc., Chem. Commun., 1980, 796; B. K. R. Shankar and H. Shechter, Tetrahedron Lett., 1982, 2277; M. Onaka, H. Kita, and Y. Izumi, Chem. Lett., 1985, 1895.

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