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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 oneelectron oxidation of diazo-compounds. The preference of cisstilbene 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)}

However, the keypoint reaction of 1^{\ddagger} 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 $1a^{\ddagger}$ to 1a to yield a diazenyl radical (3), followed by its cyclization to a tetrazine (4).



But the scheme became unlikely since it was recently established that aliphatic diazenyls are quite unstable and eliminate nitrogen much faster than their intra-molecular 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⁺ 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 $1d^{\dagger}$ and 1d is significantly reduced for the coupling between 1d[†] and 1a or 1a[†] 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-

Diazoalkane (R)	Oxidants (equiv.)	Ph(R)C=C(R)Ph (cis/trans)		(%) Other products (%) $\begin{pmatrix} Ph \\ C=N \end{pmatrix}_2 Ph CHOH Ph CHNHAC \\ R R R \end{pmatrix}$			others
1a (R=H)	Cu ²⁺ (0.015) 97	(3.6)	<1	0	0	
	Ar ₃ N ⁺ (0.022) 98	(3.8)	<1	0	0	
	Electrolysisb) 97	(4.2)	<1	0	0	
1b (R=Rh)	Cu^{2+} (0.082) 76		5	0	0	
	Ar_3N^{\ddagger} (0.12)	82		<1	0	0	
	Electrolysisb) 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 ₃ N [†] (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)

Table 1. Products on one-electron oxidation of $Ph(R)C=N_2^{a}$

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

b) Anodic oxidation with Pt electrode (+1.2 V vs. Ag/AgCl; 0.1 M LiClO₄).

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.



We have shown from the ESR study on diazomethane radical cations $(1^{+})^{6}$ that the HOMO of 1 is transformed into the LUMO of 1⁺ (see Scheme 1).⁹⁾ The frontier molecular orbital theory¹⁰⁾ tells that an ideal situation for orbital interaction between two molecules is achieved if interacting HOMO and LUMO are identical or This situation may be realized in the close to each other in orbital energy. present case between 1-HOMO and 1⁺-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^{\ddagger} 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 1^{+} .

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