1a was prepared from dry acetone, ethylene glycol, and TSA at room temperature for 12 h followed by addition of K_2CO_3 and fractional distillation,[19] and compound **10c** was prepared from 3,3-dimethyl-2-butanone and triethyl orthoformate in absolute ethanol in the presence of TSA.[20] The acetals **1f** and **10a** were of commercial origin. TCBQ was a recrystallized commercial sample. Mass spectrum of **1c**: 129 (75), 99 (4), 87 (100), 57 (10), 43 (40), 32 (65).

Photochemical Reactions. A solution of TCNB (100 mg, 0.01 M) in 60 mL of MeCN was placed in round quartz tubes and degassed by flushing with purified argon. The amount of acetal required for making the solution 0.05 M was then added, and after brief purging, the serum-capped tubes were irradiated for 0.5–3 h by means of a multilamp apparatus fitted with six 15-W phosphor-coated lamps (emission centered at 320 nm). The solvent was evaporated, and the residue bulb-to-bulb distilled under reduced pressure (50 mmHg) in order to isolate excess acetal and the 2-hydroxyethyl aliphatic esters. The residue was then submitted to flash chromatography in order to separate the alkylated aromatic nitriles by eluting with a cyclohexane–ethyl acetate mixture of increasing polarity. Further thin-layer chromatography was required for the more complicate mixtures. In the case of **1d**, a much easier separation was obtained when the esters had been previously trans esterified by brief refluxing in methanol in the presence of hydrochloric acid.

Identification of the Photoproducts. The structures of the alkylbenzenenitriles **2**, **5**, **6**, **8**, and **9** were assigned on the basis of elemental analysis and spectroscopic characteristics. The most significant features are reported in Tables V and VI. Each of the hydroxyethyl esters **5g**, **6g**, and **8g** was obtained as an oil not completely free of the other isomers; however, the NMR spectrum of each fraction was sufficiently clean to allow identification. The aliphatic hydroxyalkyl esters **3a** and **3d** are known compounds and are identical to samples prepared by synthesis;[21,22] **3d** was also converted to methyl hexanoate. The ortho ester **12′** was recognized by comparison with a sample prepared through an unambigous synthesis. The imino ester hydrochloride MeC(OMe)=NH·HCl (5 g),[23] ethylene glycol (2.8 mL), and K_2CO_3 (1 g) in anhydrous MeCN (50 mL) were stirred at 40–50 °C for 6 h. The reaction course was followed by VPC. Some K_2CO_3 was added, the salt was filtered, and the liquid distilled under reduced pressure (50 mmHg) to yield the ester **12′** (3.1 g): NMR δ 2.05 s, 3.3 s, 4.1 AB system.

Quantum Yield Determination. Experiments for quantum yield determination were carried out either in quartz tubes placed in a rotating merry-go-round and illuminated by means of a multilamp apparatus as above or in spectrophotometric cuvettes irradiated by means of a focalized Osram 150-W high-pressure mercury arc fitted with an interference filter centered at 313 nm. Reagents consumption and product formation were determined by VPC (after conversion of the 2-hydroxyethyl to methyl ester when appropriate).

Acknowledgment. This work was supported by Consiglio Nazionale delle Ricerche, Rome.

Registry No. **1a**, 2916-31-6; **1b**, 937-94-0; **1c**, 6135-54-2; **1d**, 177-10-6; **1e**, 17155-64-5; **1f**, 646-06-0; **1i**, 139071-38-8; **1j**, 15144-28-2; **2a**, 88830-20-0; **2b**, 139071-39-9; **2c**, 132381-82-9; **2e**, 139071-45-7; **2g**, 139071-41-3; **2h**, 139071-44-6; **2i**, 139071-47-9; **2j**, 132381-83-0; **3a**, 542-59-6; **3i**, 139071-49-1; **4b**, 110-54-3; **5c**, 139071-40-2; **6c**, 139100-52-0; **6h**, 139071-43-5; **7h**, 106-73-0; **8h**, 139071-44-6; **9**, 139071-46-8; **10a**, 77-76-9; **10c**, 52162-28-4; **11a**, 67-64-1; **11b**, 111-13-7; **11c**, 75-97-8; **11e**, 97-96-1; **11f**, 50-00-0; **11i**, 14113-98-5; **11j**, 3664-60-6; **13**, 139071-48-0; **14**, 132381-84-1; **15**, 96-37-7; 1,2,4,5-benzenetetracarbonitrile, 712-74-3; pyromellitic acid, 89-05-4; urea, 57-13-6; 1,2,4,5-benzenetetraamide, 6183-35-3; acetone, 67-64-1; 3,3-dimethyl-2-butanone, 75-97-8; triethyl orthoformate, 122-51-0.

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Formation and Reactivity of σ-Radical Cation Intermediates in the C–C Coupling Reaction of Phenyldiazomethanes by One-Electron Oxidation

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Received December 23, 1991

One-electron oxidation of phenyldiazomethanes afforded *cis*-stilbene predominantly. The reaction was independent of the oxidation methods, e.g., electrolysis, copper(II), triarylaminium salts, or photosensitized one-electron oxidations. The C–C coupling reaction was retarded by introducing α-substituents on phenyldiazomethane. The ESR spectra of diazoalkane radical cations could be obtained during the electrolysis at low temperature and the resulting spectra revealed their unique electronic structure as σ-radicals for most cases. When a bulky *tert*-butyl group was substituted, the corresponding π-radical cation was observed, but the C–C coupling reaction did not occur. The novel HOMO–LUMO switching by one-electron removal from the HOMO π-orbital of diazomethane is explained by the interaction of phenyl group with the C–N–N σ-radical moiety. The C–C coupling reaction proceeds via facile [4 + 2] cycloaddition between the diazomethane and σ-radical cation, and the preferential formation of *cis*-olefins is based on the secondary orbital interaction between the two phenyl groups. The structure and the stability of radical cation intermediates are rationalized on the basis of ab initio calculations.

Introduction

Dimerizations of diazoalkanes affording olefins or azines are well-known and are mostly explained as carbenoid reactions catalyzed by metallic salts.[1] These reactions are not always useful because of formation of product mixtures involving olefins, azines, glycols, and ketones. An exceptionally clean reaction has been reported for the oxidation of diphenyldiazomethane; the corresponding dimeric olefin was obtained in high yields by the anodic oxidation[2] and

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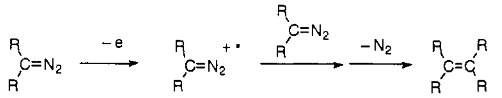
0022-3263/92/1957-3057$03.00/0

Table I. Products of the One-Electron Oxidation of Phenyldiazomethane (1a)[a]

run no.	solvent	temp (°C)	oxidants (equiv)[b]	products (%) PhCH=CHPh	products (%) others
		A. Oxidation under Argon			
1	MeCN	20	electrolysis	97 (4.2)	
2			Cu^{2+} (0.015)	97 (3.6)	
3			$Ar_3N^{+\bullet}$ (0.022)	98 (3.9)	
4			DCA/$h\nu$[c]	98 (3.1)	
5			$h\nu$[d]	9 (0.8)	$(PhCH{=}N)_2$, 10
6	$MeCN-CH_2Cl_2$ (1:2)	−78	Cu^{2+} (0.05)	91 (9.9)	
7			$Ar_3N^{+\bullet}$ (0.05)	68 (8.6)	
8			DCA/$h\nu$[c]	84 (6.0)	
9	MeCN–MeOH (9:1)	20	electrolysis	93 (4.2)	$PhCH_2OMe$, 1
10			Cu^{2+} (0.015)	92 (4.1)	$PhCH_2OMe$, 1
11			$Ar_3N^{+\bullet}$ (0.022)	75 (4.0)	$PhCH_2OMe$, 2
12			DCA/$h\nu$[c]	78 (3.3)	$PhCH_2OMe$, 5
13			$h\nu$[d]	5 (0.7)	$PhCH_2OMe$, 87
		B. Oxidation under Oxygen			
14	MeCN	20	electrolysis	100 (4.2)	PhCHO, <1
15			Cu^{2+} (0.015)	90 (4.6)	PhCHO, <1
16			$Ar_3N^{+\bullet}$ (0.022)	76 (3.5)	PhCHO, 4
17			DCA/$h\nu$[c]	<1	PhCHO, 95

[a] A 3–10-mL solution of 3–4 mM **1a** was oxidized. After the completion of reaction, products were determined by GLC. [b] DCA/$h\nu$: irradiation at >400 nm in the presence of 0.4 mM DCA for 1.5 h. Electrolysis: anodic oxidation with a Pt electrode and 0.1 M $LiClO_4$ at +1.2 V vs Ag/AgCl. Cu^{2+} and $Ar_3N^{+\bullet}$: oxidation with copper(II) perchlorate and tria(*p*-bromophenyl)aminium hexachloroantimonate, respectively. Values in parentheses are molar equiv vs **1a**. [c] Irradiation for 15 min. [d] Direct irradiation (16 h) in the absence of DCA.

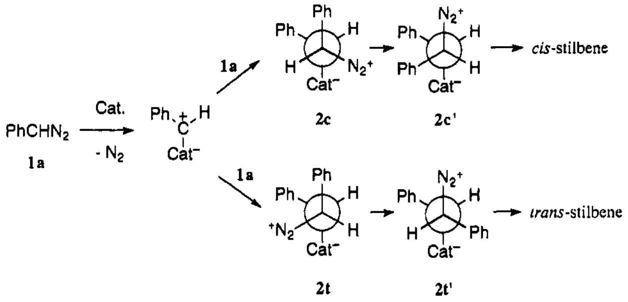
by the oxidation with copper(II) or aminium salts.[3] These results suggested a mechanism involving radical cations (eq 1). However, a recent careful study by Bethell and Parker has demonstrated that the olefin is produced by H^+-catalyzed decomposition of the diazomethane since the reaction was inhibited by the addition of pyridines.[4]



(1)

The formaton of dimeric olefins from phenyldiazomethane (**1a**) has been studied extensively on the catalytic reaction using ceric[5] and cupric salts,[6] lithium bromide,[7] rhodium complex,[8] and chloranil.[9] Of interest here is that *cis*-stilbene was formed in preference to the more stable trans isomer. Although a chain scheme like eq 1 involving radical cation ($1a^{+\bullet}$) was proposed for the case of cerium(IV),[5] an alternative carbenoid mechanism as shown in Scheme I has often been written for these reactions.[6,8,9] The explanation for the predominant formation of *cis*-stilbene here is based on the assumptions that (i) the initial adduct **2c** is sterically more stable than **2t** and that (ii) stilbenes are formed from **2c′** and **2t′** by the trans elimination of catalyst and nitrogen. This scheme is supported by the fact that the resulting cis/trans ratios of stilbenes are affected by the bulkiness of metal ligands. Involvement of radical cations from phenyldiazomethanes has not been clarified but seems to be feasible when their one-electron oxidation is thermodynamically favorable.

Scheme I



The reactivity of diazoalkane radical cations has not been thoroughly understood. Few examples include the dimer formation from radical cations of phenylmesityldiazoethane[10] and 9-diazofluorene.[11] An interesting elimination of nitrogen to yield cationic carbenes from diazomethane radical cations has been proposed in anodic oxidation[12] and evidenced by a first-order decay of the radical cations.[13] Such decay kinetics may be explicable also in terms of a transformation between different electronic structures of radical cations.[14]

It is apparent from the present short review that the formation, structure, and reactivity of diazoalkane radical cations are not thoroughly understood. Herein, we wish to summarize our mechanistic study on the C–C coupling reaction by the one-electron oxidation of aryldiazomethanes. Interest is focussed on the electronic structure and reactivity of diazomethane radical cations involved. Preliminary results have been reported on the predominant formation of *cis*-stilbene by typical one-electron methods[15] and the ESR spectra of radical cation intermediates at low temperature.[16]

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Table II. One-Electron Oxidation of Substituted Phenyldiazomethanes 1b–e[a]

diazo compound	E_p^{ox} (V vs Ag/AgCl)[c]	condtns (equiv)[b]	convsn (%)	products (%) ArCH=CHAr (cis/trans)
(p-ClC_6H_4)CHN_2 (**1b**)	1.20	DCA/$h\nu$[d]	100	94 (2.9)
		Cu^{2+} (0.077)	100	89 (3.6)
		$Ar_3N^{+\bullet}$ (0.10)	100	85 (2.9)
(p-MeC_6H_4)CHN_2 (**1c**)	0.86	DCA/$h\nu$[e]	70	82 (3.3)
(o-MeC_6H_4)CHN_2 (**1d**)	0.88	DCA/$h\nu$[e]	61	78 (1.5)
		Cu^{2+} (0.15)	100	81 (1.9)
(p-$MeOC_6H_4$)CHN_2 (**1e**)	0.84	DCA/$h\nu$[e]	53	70 (3.1)

[a] A 3–8 mM solution of 1 in acetonitrile was oxidized under argon at 20 °C. Products were determined by GLC. [b] See footnote *b* of Table I. [c] Peak potential for the oxidation of 1 determined in MeCN by cyclic voltammetry; 1–5 mM 1, 0.1 M $LiClO_4$; 100 mV/s. [d] Irradiation for 1.5 h. [e] Irradiated for 5 h.

Results

One-Electron Oxidation of Phenyldiazomethane. Four types of oxidation methods have been applied for the one-electron oxidation of diazomethanes, i.e., an anodic reaction, photosensitization, cupric ion, and triarylaminium ion oxidations.

The cyclic voltammogram of phenyldiazomethane (**1a**) in acetonitrile (0.1 M $LiClO_4$, 100 mV/s) was irreversible, the anodic peak potential (E_p^{ox}) being +0.94 vs Ag/AgCl. When **1a** was electrolyzed anodically in acetonitrile using Pt electrodes at +1.2 V vs Ag/AgCl under argon, stilbene as a sole C–C coupling dimer was obtained almost quantitatively and the predominant product was the cis isomer, the cis/trans ratio being as high as 4. Similar results were obtained by oxidation with a catalytic amount of copper(II) perchlorate ($E_{1/2}^{red}$ = +1.0 V vs SCE)[3] or tris(4-bromophenyl)aminium hexachloroantimonate ($E_{1/2}^{red}$ = +1.04 V vs SCE)[17] as shown in Table I, part A. The successful dimerization with catalytic amounts of oxidants is indicative of the chain nature of the reaction. This was confirmed by the fact that the current efficiency increased from 7.5 to 39 mol/F as the concentration of **1a** increased from 4.5 to 16 mM.

The photochemical one-electron oxidation was examined using 9,10-dicyanoanthracene (DCA) as a typical sensitizer. When **1a** and DCA were irradiated in acetonitrile under argon, *cis*- and *trans*-stilbenes were obtained with a similar cis/trans ratio (run no. 4 in Table I, part A). The observed diffusion-controlled quenching of DCA fluorescence is understood since the reduction potential of excited ^{1}DCA is +2.86 vs SCE[18] and enough to oxidize **1a** (E_p^{ox} = +0.94 V) effectively. When **1a** was directly irradiated in the absence of DCA to yield carbene intermediates (run no. 5 in Table I), low yields of stilbenes (total 9%, cis/trans = 0.8) and benzalazine, PhCH=NN=CHPh, were obtained as volatile products. This result means that phenylcarbene is not involved in the efficient formation of *cis*-stilbene; the azine formation by C–N coupling is one of typical reactions of carbenes.

For examination of a possible intermediacy of phenylcarbene or its cation in the efficient *cis*-stilbene formation, the reaction was conducted in the presence of 10% methanol. As shown in runs 9–12 in Table I, the olefin formation was not affected by methanol and the yields of phenyl methyl ether were negligibly low (i.e., <5%). Since the reactions of arylcarbenes and methanol are close to the diffusion-controlled rate,[19] phenylcarbene is not involved in the present C–C coupling. In fact, when phenylcarbene was produced by the direct irradiation of **1a** (run no. 13), the methyl ether was obtained predominantly. It is also apparent that the corresponding carbene cation ($PhCH^{+\bullet}$), which would be more electrophilic and trapped efficiently by methanol, is not involved in the C–C coupling.

$$\underset{\mathbf{1a}}{PhCHN_2} \xrightarrow[\text{MeOH–MeCN}]{-e} \mathbf{1a}^{+\bullet} \xrightarrow{\mathbf{1a}} \underset{\text{cis} \gg \text{trans}}{PhCH{=}CHPh} \quad (2)$$

$$\underset{\mathbf{1a}}{PhCHN_2} \xrightarrow[\text{MeOH–MeCN}]{h\nu} PhCH: \xrightarrow{\text{MeOH}} PhCH_2OMe \quad (3)$$

Care should be taken since radical cation reactions sometime involve an acid-catalyzed process.[20] Thus, the present one-electron oxidation of phenyldiazomethane (**1a**) was examined in the presence of 0.1 M 2,6-di-*tert*-butylpyridine in acetonitrile. The olefin formation was not affected by the pyridine base. On the other hand, the acid-catalyzed decomposition of **1a** with 2.0 × 10^{-4} M $HClO_4$ in MeCN afforded a complex miture of $PhCH_2NHCOMe$, $PhCH_2OH$, and a small amount of stilbenes (trans ≫ cis); the same reaction in MeOH–MeCN (1:9) yielded $PhCH_2OMe$ quantitatively. Hence, it is concluded that acid-catalyzed reaction is not involved in the predominant formation of *cis*-stilbene.

The reaction of **1a** by one-electron oxidation was not affected by the presence of oxygen. As shown in runs 14–16 in Table I, part B, high yields of *cis*-stilbene were obtained under oxygen and the yield of benzaldehyde was low (i.e., <5%). These facts indicate that the radical cation intermediates (e.g., $\mathbf{1a}^{+\bullet}$) do not react with oxygen. An exceptional case was the DCA-sensitized reaction, affording benzaldehyde (run no. 17 in Table I, part B) presumably via a carbonyl oxide intermediate ($PhCH{=}O^+{-}O^-$, 3),[21] which may be generated by the reaction of $\mathbf{1a}^{+\bullet}$ with $O_2^{-\bullet}$ or, more likely, by the oxidation of **1a** with singlet oxygen.[22]

These experiments under various conditions clearly demonstrated that the efficient stilbene formation proceeds by way of a radical chain mechanism involving diazomethane radical cation $\mathbf{1a}^{+\bullet}$. The reaction was likewise effective at lower temperature and the resulting cis/trans ratio was as high as 9 at −78 °C (Table I, part A, runs 6–8).

Substituted Phenyldiazomethanes. The one-electron oxidation of ring-substituted phenyldiazomethanes **1b–e** afforded substituted stilbenes similarly with cis/trans ratios of 2–4 (Table II). The ratios for **1d** (o-Me) were

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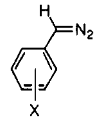
[22] (a) The simultaneous generation of $O_2^{-\bullet\,22b}$ and $^1O_2^{\,22c}$ in DCA-sensitized photooxidations is well established. (b) Spada, L. T.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 39. (c) Dobrowski, D. C.; Obilby, P. R.; Foote, C. S. *J. Phys. Chem.* **1983**, *87*, 2261.

Table III. Cross Products from the Oxidation of Mixtures of Diazomethanes[a]

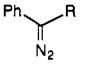
diazo compds 1 + Ar(R)CN$_2$	conditions[b]	stilbenes, % (cis/trans) Ar'CH=CHAr'	 Ar'CH=C(R)Ar	 Ar(R)C=C(R)Ar	others	rel rate[c] Ar(R)CN$_2$/1a
A. Cooxidation of **1a** (Ar' = Ph) and **1b** (Ar = *p*-ClC$_6$H$_4$, R = H)[d]						
1a + **1b**	DCA/$h\nu$	27 (3.6)	35 (2.9)	29 (3.1)		0.8
1a + **1b**	Ar$_3$N$^{+\bullet}$	21 (3.6)	42 (3.0)	28 (3.0)		0.9
B. Cooxidation of **1a** (Ar' = Ph) and **4b** (Ar = Ph, R = Et)[e]						
1a + **4b**	DCA/$h\nu$	31 (3.1)	7 (1.8)	<1	*f*	0.4
C. Cooxidation of 1 and 6 (Ar = Ph, R = Ph)						
1a (Ar' = Ph) + **6**[g]	Ar$_3$N$^{+\bullet}$	35 (2.6)	<1	<1	*h*	<0.1
1b (Ar' = *p*-ClC$_6$H$_4$) + **6**[i]	Ar$_3$N$^{+\bullet}$	49 (2.9)	<1	<1	*j*	<0.1

[a] An approximately equimolar mixture of two diazomethanes was oxidized in MeCN under argon. After the completion of reaction, products were determined by GLC. Yields are based on the total amount of the diazoalkanes. [b] See footnote *b* in Table I. [c] Relative oxidation rates of diazoalkanes as determined at low conversion of ~25%. [d] A mixture of 5.0 mM **1a** and 5.5 mM **1b**. [e] A mixture of 3.0 mM **1a** and 3.2 mM **4b**. [f] PhCH=CHMe (35%, cis/trans = 0.22); PhCH=NN=C(Et)Ph (15%). [g] A mixture of 17.4 mM of **1a** and 26.8 mM of **6**. [h] **6** (55%). [i] A mixture of 12.1 mM of **1b** and 10.0 mM of **6**. [j] **6** (38%).

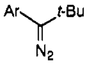
significantly lower than those of other substituents. Another interesting point in the table is that the DCA-sensitized photooxidation of **1c–e** with an electron-donating group was much slower than that of **1a** or **1b** (*p*-Cl). An explanation for the reversed reactivity of 1's with lower oxidation potentials (cf. Table II) is that back electron transfer within ion pairs ($1^{+\bullet}/DCA^{-\bullet}$) becomes faster with decreasing exothermicity; such cases have recently been reported for several ion pairs.[23]



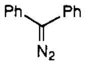
1a : X = H
1b : X = *p*-Cl
1c : X = *p*-Me
1d : X = *o*-Me
1e : X = *p*-MeO



4a : R = Me
4b : R = Et



5a : Ar = Ph
5b : Ar = *p*-MeC$_6$H$_4$
5c : Ar = *p*-MeOC$_6$H$_4$



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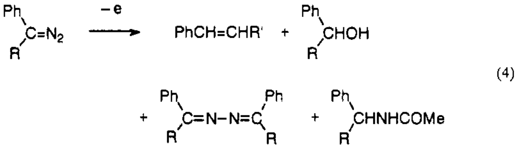
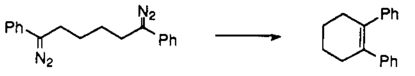
The yields of dimeric olefins were quite low for the phenylalkyldiazomethanes. The major products from the one-electron oxidation of 1-phenyldiazoethane (**4a**) or 1-phenyl-1-diazopropane (**4b**) under the same conditions were styrenes, alcohols, azines, and amides (eq 4). Similarly, the electrolysis of phenyl-*tert*-butyldiazomethane (**5a**) afforded Ph(Me)C=CMe$_2$ (20%), Ph(*t*-Bu)CHOH (12%), Ph(*t*-Bu)CHNHCOMe (23%), and the azine (14%). However, these were regarded as products via the H$^+$-catalyzed decomposition, since the catalytic reaction was reduced by the addition of 0.1 M 2,6-di-*tert*-butylpyridine. In the presence of base, the reaction was completed only by equivalent amounts of oxidants or with the current efficiency of ~1 F/mol, however, resulting in the formation of complex product mixtures. These results indicate that the C–C coupling reaction via radical cation $4^{+\bullet}$ or $5^{+\bullet}$ is quite inefficient owing to the steric hindrance by the α-alkyl groups. This is in line with the fact that DCA-sensitized reaction of 4 was quite inefficient under conditions similar to those in the case of **1a**. As reported by Parker and Bethell,[4] the formation of Ph$_2$C=CPh$_2$ in the one-electron oxidation of diphenyldiazomethane (**6**) is not via the radical cation pathway but via a H$^+$-catalyzed reaction. This is because the olefin formation was completely inhibited by the addition of 2,6-di-*tert*-butylpyridine (0.1 M). The attempted DCA-sensitized reaction of **6** did not yield the dimeric olefin. Thus, the C–C coupling reaction for **6** is also retarded by steric effect of another phenyl group.



(4)

The above-mentioned results indicate that the C–C coupling reaction is subject to a significant steric retardation and is inhibited by α-alkyl or α-phenyl groups on phenyldiazomethanes. Such a steric inhibition may be reduced when the C–C coupling proceeds intramolecularly. Thus, the C–C-coupled olefin **8** was obtained quantitatively (over 95%) from bis-diazo compound **7** by one-electron oxidation with cupric perchlorate or by DCA-sensitized irradiation (eq 5).



7 8 (5)

Cross-Coupling Reactions. The extent of steric hindrance for the C–C couplings was examined in the cross reactions between 1 and other diazomethanes. When the one-electron oxidation was conducted for a 1:1 mixture of **1a** and **1b** (*p*-Cl), the corresponding homocoupled and cross-coupled stilbenes were obtained in almost statistical product ratio as listed in Table III, part A. The relative reaction rates for **1a** and **1b**, determined at low conversions below 25%, were almost the same. This indicates that radical cation intermediates react with **1a** and **1b** with no selectivity.

The DCA/$h\nu$ oxidation of a mixture of **1a** and **4b** afforded a small amount of the cross dimer in addition to stilbene as the homodimer from **1a** (Table III, part B). The relative consumption rate of **1a** and **4b** at the initial stage of reaction was 2.3:1. The evaluation of these relative rates is rather complex since it is not easy to distinguish the net coupling either from $1a^{+\bullet}$ and **4b** or from $4b^{+\bullet}$ and **1a**.

In the arylaminium oxidation of the mixture of **1a** (E_p^{ox} = +0.94 V) and **6** (E_p^{ox} = +1.00 V vs Ag/AgCl), **1a** was selectively consumed and the resulting olefin was stilbene only; the crossed olefin could not be detected (Table III, part C). Likewise, no cross olefin was obtained on the one-electron oxidation of **6** and **1b** (E_p^{ox} = +1.2 V). Thus, cross-coupling does not occur between 1 and 6 regardless of their oxidation potentials.

ESR Spectra Obtained by in Situ Electrolysis of Diazomethanes. In order to detect diazomethane radical

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(23) Mataga, N.; Asahi, T.; Kanda, Y.; Okada, T.; Kakitani, T. *Chem. Phys.* **1988**, *127*, 24. Vauthey, E.; Suppan, P.; Haselbach, E. *Helv. Chim. Acta* **1988**, *71*, 93. Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 429.

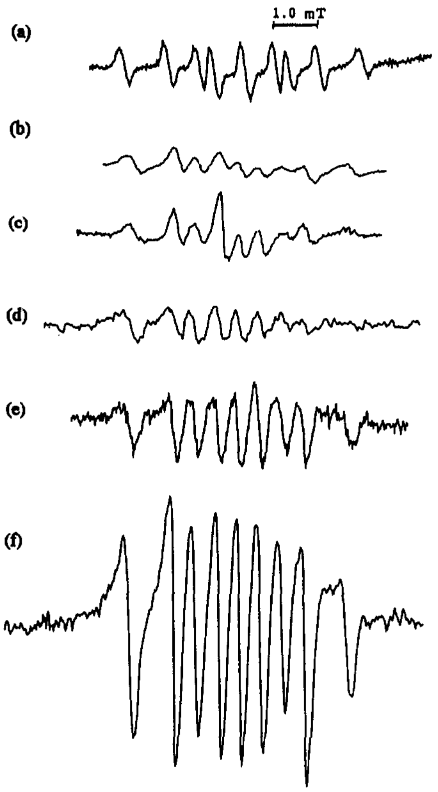


Figure 1. ESR spectra observed during the electrochemical oxidation of (a) **6**, (b) **1a**, (c) **1b**, (d) **1d**, (e) **4a**, and (f) **4b** at −33 to −90 °C in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4.

cations, we attempted to obtain ESR spectra during the anodic oxidation in the cavity. Although the attempt was unsuccessful in solutions of MeCN or MeCN–CH_2Cl_2, the ESR spectra of radicals could be obtained by the in situ electrolysis of 20–40 mM solution of diazoalkanes in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4 at low temperature. The resulting spectrum from **6** during the electrolysis at +1.3 V vs Ag/AgCl is shown in Figure 1, spectrum a. The triplet of triplets pattern is due to the hyperfine couplings with two nonequivalent nitrogens with considerably large coupling constants, 1.72 and 1.01 mT. When the electrolysis was stopped, this species decayed with half-lives of ~10 s at −33 °C and ~90 s at −83 °C. Similar spectra were obtained from **4a** and **4b** as shown in Figure 1, spectra e and f, respectively, their half-lives being as short as ~1 s at −90 °C.

The ESR spectrum from phenyldiazomethane (**1a**) could not be observed under the same conditions. However, a very weak nine-peak signal as shown Figure 1, spectrum b, could be observed only if a much higher voltage (e.g., up to 6 V) was applied for the concentrated solution of **1a** (up to 0.5 M) at −90 °C, revealing the much higher reactivity of the species compared to those from **6** and **4**. The resulting hyperfine coupling constants, 1.47 and 1.03 mT, of two nitrogen atoms were practically identical to those from **4a**, **4b**, or **6**. Similar spectra were obtained from **1b** and **1d** as shown in Figure 1, spectra c and d. For the cases of **1c** and **1e**, ESR signals could not be obtained even under the extreme conditions.

ESR signals could not be observed from phenyl-*tert*-butyldiazomethane (**5a**) with the bulky *tert*-butyl substituent. As demonstrated in the one-electron oxidation of phenylmesityldiazoethane by Little and Schuster,[10] the resulting diazoalkane radical cations are known to afford dimeric products by coupling at the para position of the phenyl group. The same type of reaction may be a reason for no observation of ESR signals from **5a**. Then the *p*-methyl derivative **5b** was examined, and a quite different type of spectrum was observed as shown in Figure 2, spectrum a. This radical was notably long-lasting, the half-life being as long as 10 min at −90 °C. This well-resolved spectrum could be nicely reproduced by using the hyperfine couplings of nitrogen and hydrogen atoms of **5b** (Figure 2, spectrum b): two nonequivalent nitrogens (0.47 and 0.35 mT), two ortho hydrogens (0.35 mT), two meta hydrogens (0.08 mT), and three hydrogens on a methyl group (0.67 mT). Similarly, the *p*-methoxy derivative **5c** afforded a more stable radical with a half-life of ~30 min at −90 °C, and its ESR spectrum (Figure 2, spectrum c) could be simulated by using the coupling constants of two nitrogens (0.39 and 0.34 mT), two ortho hydrogens (0.33 and 0.26 mT), and methyl hydrogens (0.14 mT). The resulting ESR data are summarized in Table IV.

Discussion

Electronic Structure of Diazomethane Radical Cations. The removal of one electron from the π-orbital (HOMO) of phenyldiazomethanes[24] produces a π-radical

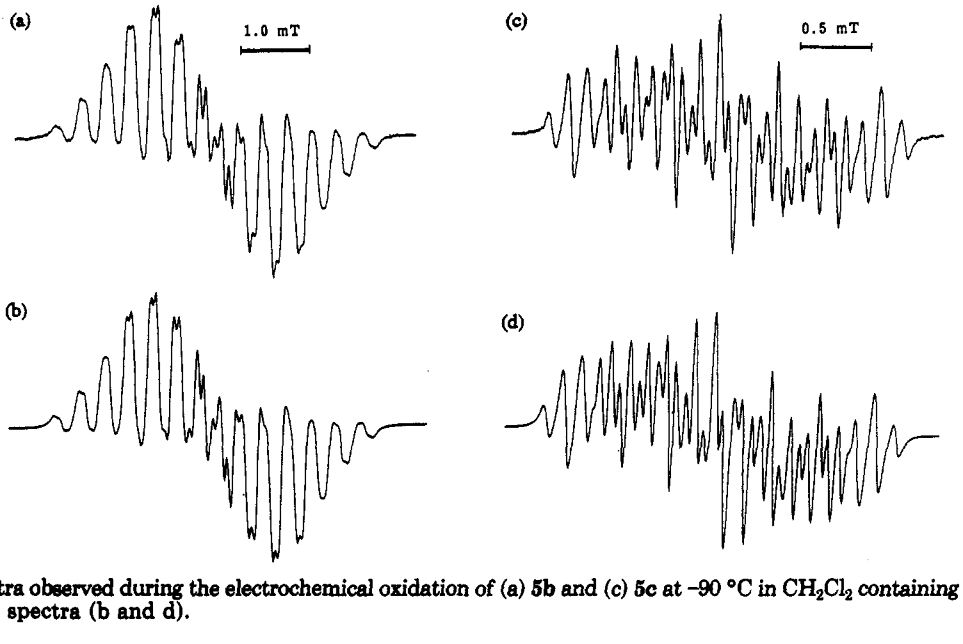


Figure 2. ESR spectra observed during the electrochemical oxidation of (a) **5b** and (c) **5c** at −90 °C in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4 and their simulated spectra (b and d).

Table IV. ESR Spectral Data for Diazoalkane Radical Cations[a]

diazo compound	a_N (mT)[b]	a_H (mT)[c] ortho H	a_H (mT)[c] meta H	a_H (mT)[c] CH_3	g[d]	electronic structure assigned
$PhCHN_2$ (**1a**)	1.47 ± 0.03, 1.03 ± 0.02				2.0008 ± 0.0002	σ
p-$ClC_6H_4CHN_2$ (**1b**)	1.48 ± 0.02, 1.01 ± 0.02				2.0014 ± 0.0002	σ
o-$MeC_6H_4CHN_2$ (**1d**)	1.50 ± 0.02, 1.02 ± 0.02				2.0017 ± 0.0001	σ
$Ph(Me)CN_2$ (**4a**)	1.49 ± 0.02, 1.01 ± 0.02				2.0015 ± 0.0002	σ
$Ph(Et)CN_2$ (**4b**)	1.48 ± 0.02, 1.01 ± 0.03				2.0016 ± 0.0001	σ
Ph_2CN_2 (**6**)	1.72 ± 0.01, 1.01 ± 0.01				2.0009 ± 0.0001	σ
p-MeC_6H_4(t-Bu)CN_2 (**5b**)	0.47,[c] 0.35[c]	0.35 (2 H)	0.08 (2 H)	0.67 (3 H)	2.0017 ± 0.0001	π
p-$MeOC_6H_4$(t-Bu)CN_2 (**5c**)	0.39,[c] 0.34[c]	0.33 (1 H) 0.26 (1 H)		0.14 (3 H)	2.0021 ± 0.0001	π

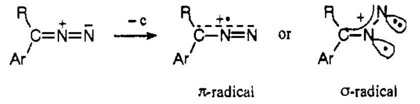
[a] Generated in an ESR cavity by electrolysis of 20–500 mM diazoalkane in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4 under Ar at −60 to −90 °C. [b] Coupling constants. [c] Simulated coupling constants. [d] g value.

Table V. Calculated Total Energies of π- and σ-Radical Cations for H_2CN_2 and $PhCHN_2$[a]

	UHF/STO-3G	MP2/STO-3G[b]
$H_2CN_2^{+\bullet}$		
π-radical	−145.742362	−145.858985
σ-radical	−145.656762	−145.774089
ΔE (kcal/mol)[c]	+53.7	+53.3
$PhCHN_2^{+\bullet}$		
π-radical	−372.569468	−372.967357
σ-radical	−372.555714	−372.967440
ΔE (kcal/mol)[c]	+8.6	−0.1

[a] Optimized geometries are shown in Figure 4. [b] Calculated at UHF/STO-3G optimized geometry. [c] The energy difference: $E(\sigma\text{-radical}) - E(\pi\text{-radical})$.

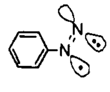
cation with a linear C–N–N geometry in which the unpaired electron is delocalized over the allylic π-system and the phenyl ring. An alternate electronic structure is also conceivable which has a bent C–N–N geometry and localized unpaired electron on the two nitrogen atoms, i.e., a σ-radical structure (eq 6).[25]



(6)

Two types of ESR spectra were obtained on anodic oxidation of diazoalkanes; one showed large hyperfine couplings of two nitrogen atoms only and the other was a well-resolved pattern resulting from the mixing of smaller couplings of both nitrogens and hydrogens on the Ar group (e.g., Figure 2). The latter type was obtained when R = t-Bu and is apparently ascribed to a π-radical structure, since the unpaired electron is delocalized over the diazo and phenyl groups. In fact, the π-radical structure from **5b** is well reproduced by coupling constants of two nitrogens and three types of seven hydrogens as exemplified in Figure 2, spectrum b. A similarly complex spectrum was obtained from p-methoxy isomer **5c** and was simulated adequately by the coupling constants in Table IV.

On the other hand, the simpler ESR spectra were obtained from **1a,b,d** (R = H), **4a,b** (R = Me, Et), and **6** (R = Ph) as shown in Figure 1. The coupling of any hydrogen atom on Ar or R group was not observed in these spectra. The coupling constants of two nitrogen atoms (i.e., 1.5–1.7 and 1.0 mT) are practically unchanged by substituents on Ar or R groups as listed in Table IV and are close to those (2.25 and 0.94 mT) of phenyldiazenyl (**9**), a reported σ-radical.[27c] Thus, these species from phenyldiazomethanes seem to have a σ-radical structure with unpaired electrons on the two nitrogens, which can be assigned to the corresponding σ-radical cations. The assignments of σ-radical structure are discussed below.



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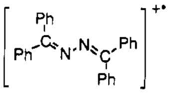
(1) Various types of radical intermediates possessing two nitrogen atoms are conceivable and shown in **10**–**15**; none of these species satisfies the present observation. Benzophenone azine radical cation (**10**),[28] hydrazonyl radicals (**11**),[29] and hydrazone radical cations (**12**)[30] have been reported to have hyperfine coupling constants quite different from the present ones. Diazenyl radical **13** may have similar coupling constants, but the lifetime of it is assumed to be too short for ESR observation; the lifetimes of aliphatic diazenyls such as **13** are 10^{-10} s at room temperature[31a] and are predicted to be much shorter than 10^{-7} s at −83 °C since the activation energies for decomposition of aliphatic diazenyls are less than 6.6 kcal/mol.[31b] Dimeric 1,1-diazene radical cations **14** and **15** proposed by Bethell et al.[3] are considered to have a localized spin density on one nitrogen atom and a hyperfine coupling constant similar to the case of iminyl radicals $R_2C{=}N^\bullet$ (i.e., ~1.0 mT).[32] These were not the case.



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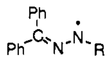

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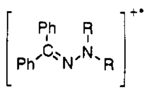

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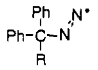

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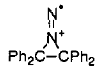

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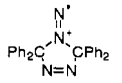

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(24) (a) Moffat, J. B. *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: New York, 1978; Chapter 1. (b) Heilbronner, E.; Martin, H.-D. *Chem. Ber.* **1973**, *106*, 3376.

(25) *σ-Radicals* are defined as radicals in which the unpaired electron occupies an orbital of s character[26a] or an orbital perpendicular to the π-system of the molecule.[26b] The diazoalkane σ-radical cations, in which the odd electron resides in an sp^2-orbital on the central nitrogen, satisfies the definitions. Relevant radicals with a similar two-center three-electron bond in the molecular plane, e.g., iminoxyl,[26b,27a] benzoyl,[27b] diazenyl,[27c] and nitrosobenzene radical cation,[27d] have been reported to be σ-radicals.

(26) (a) Danen, W. C.; West, C. T. *J. Am. Chem. Soc.* **1973**, *95*, 6872. (b) Norman, R. O. C.; Gilbert, B. C. *J. Phys. Chem.* **1967**, *71*, 14.

(27) (a) Symons, M. C. R. *J. Chem. Soc.* **1965**, 2276. (b) Krusic, P. C.; Rettig, T. A. *J. Am. Chem. Soc.* **1970**, *92*, 722. (c) Suehiro, T.; Masuda, S.; Tashiro, T.; Nakausa, R.; Taguchi, M.; Koike, A.; Rieker, A. *Bull. Chem. Soc. Chem.* **1986**, *59*, 1877. (d) Cauquis, G.; Genies, M.; Lemaire, H.; Rassat, J. P. *J. Chem. Phys.* **1967**, *47*, 4642.

(28) Ho, C.-T.; Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1974**, *96*, 8109.

(29) Ahrens, W.; Berndt, A. *Tetrahedron Lett.* **1974**, 3741.

(30) Berndt, A.; Bolze, R.; Schnaut, R.; Woyner, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 390.

(31) (a) Porter, N. A.; Marnett, L. J.; Lochmüller, C. H.; Closs, G. L.; Shobataki, M. *J. Am. Chem. Soc.* **1972**, *94*, 3664. (b) Engel, P. S.; Gerth, D. B. *J. Am. Chem. Soc.* **1983**, *105*, 6849.

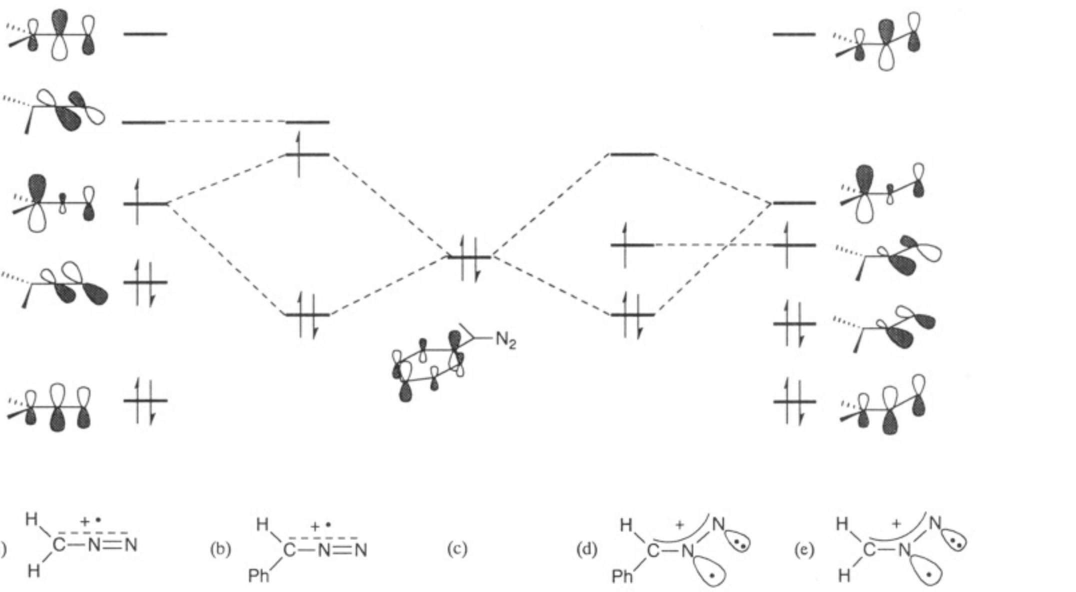

Figure 3. Schematic drawing of MOs of (a) diazomethane π-radical cations, (b) phenyldiazomethane π-radical cation, (c) HOMO orbital of Ph, (d) phenyldiazomethane σ-radical cation, and (e) diazomethane σ-radical cation.

(2) The present assignment of σ-radical structure may be justified on the basis of theoretical calculations. We calculated the electronic structures for parent diazomethane radical cation $H_2CN_2^{+\bullet}$ according to the ab initio UHF-MO method on the STO-3G basis set[33] and could find π- and σ-radical structures on the potential energy surface. The calculated π-radical cation has a linear C–N–N geometry with an odd electron in a three-centered allylic π-orbital, which corresponds to the HOMO of H_2CN_2 (see Figure 3, part a). On the other hand, the σ-radical cation takes on a planar bent geometry in which an unpaired electron is localized in the in-plane N–N orbital (see Figure 3, part e).

The resulting total energy of σ-$H_2CN_2^{+\bullet}$ was 53.7 kcal/mol higher than that of the corresponding π-radical. However, the energy difference between σ- and π-radical cations was dramatically reduced down to 8.6 kcal/mol for the case of $PhCHN_2^{+\bullet}$. By a more sophisticated MP2/STO-3G method,[34] the σ-radical structure for $PhCHN_2^{+\bullet}$ was shown to be slightly more stable than the π-structure (Table V). Although the calculated values have only a qualitative meaning,[35] it can be presumed that the energy levels of the σ- and π-radical structures are almost degenerated.

The dramatic effect of the phenyl substituent can be well understood as shown in Figure 3. When the π-SOMO (singly occupied MO) of π-$H_2CN_2^{+\bullet}$ (a) is mixed with the HOMO orbital of the phenyl group (c), the interaction stabilizes the structure of π-$PhCHN_2^{+\bullet}$ (b) moderately, but it reduces the energy gap between the SOMO and the vacant N–N antibonding orbital. In contrast, stabilization by the interaction between the HOMO of Ph (c) and the vacant π-orbital of σ-$H_2CN_2^{+\bullet}$ (e) is much more significant for the case of σ-$PhCHN_2^{+\bullet}$ (d), and the resulting energy order is reversed, leading to the observation of σ-radical cations.

(3) A question not easy to explain is why the hyperfine couplings of α-hydrogens on $\mathbf{1}^{+\bullet}$ are so small that they are not resolved, i.e., less than 0.2 mT. This result is in contrast to the case of the iminoxyl radical (PhCH=N—O•), a well characterized σ-radical, which shows relatively large α-H coupling constants, 0.65 and 2.70 mT for syn and anti forms, respectively.[36] The difference between neutral radical PhCH=N—O• and radical cation $PhCHN_2^{+\bullet}$ may be explained as follows: First, radical cations are known to form contact ion-pairs with counter anions in less polar solvents such as CH_2Cl_2. In the present case of $PhCHN_2^{+\bullet}$, the energetically favorable coordination is such that the bulky BF_4^- is located anti to the phenyl group. Also, σ-$PhCHN_2^{+\bullet}$ exists in the syn form, resulting in the lower value for α-H. Second, the spin polarization on π-orbitals induced by an unpaired electron on the σ-SOMO, which is regarded as the origin of the still large α-H coupling of *syn*-PhCH=N—O• (i.e., 0.65 mT)[36] without a trans effect on the spin transmission, is less important for the present case of $\mathbf{1}^{+\bullet}$. The spin densities on π-orbitals as calculated by UHF/4-31G[37] were much smaller for σ-$H_2CN_2^{+\bullet}$ than those for H_2C=N—O•: −0.053, −0.097, +0.150 for C, N, N of σ-H_2C-N-$N^{+\bullet}$ and −0.574, +0.493, +0.082 for C, N, O of H_2C=N—O•.[38] The sharp contrast is attributed to the number of electrons in the π-system. In the case of σ-$H_2CN_2^{+\bullet}$, two electrons in the allylic π-orbitals are of quite low energy and the exchange interaction with the σ-SOMO is negligible, while the four-π-electron system of H_2C=N—O• is subjected to a significant spin polarization due to the close energy level of upper π-orbital and σ-SOMO. Thus, the observation of a quite low hyperfine coupling constant for the α-hydrogen of σ-$PhCHN_2^{+\bullet}$ is explicable if it is in the syn form.

It is interesting to note that the one-electron oxidation from phenyldiazomethanes yields σ- or π-radical cations depending on the substituents. Hence, some should be mentioned on the relative energies and interconversion between them. It is quite natural that the one-electron

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[32] Griller, D.; Mendenhall, G. D.; van Hoof, W.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6068.

[33] Hehre, H. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1967**, *51*, 265.

[34] Pople, J. A.; Binkley, S.; Seger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.

[35] The STO-3G basis set is not accurate enough to estimate such a small difference in molecular energies, and the contamination of higher spin states is unavoidable in the present UHF calculations. However, $PhCHN_2^{+\bullet}$ is too large to be calculated with more extended basis sets.

[36] Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc.* **1966**, 86.

[37] Hehre, H. J.; Ditchfield, R.; Random, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

[38] These values are apparently too large because UHF-MO methods usually overestimate spin polarization, but the calculated result seems to explain qualitatively the difference between σ-$H_2CN_2^{+\bullet}$ and H_2C=N—O•.

removal from the π-orbital (HOMO) of diazomethanes[24] produces the corresponding π-radical cations. In fact, π-radical cations were detected from phenyl-*tert*-butyldiazomethanes **5b**,**c**. However, σ-radical cations were observed for most cases, e.g., $\mathbf{1}^{+\bullet}$, $\mathbf{4}^{+\bullet}$, and $\mathbf{6}^{+\bullet}$, demonstrating clearly the turnover of SOMO from π- to σ-orbitals. This indicates that the energy levels of σ-SOMOs are lower than those of the π-SOMOs for these cases and the transformation from π- to σ-structure is facile. The exceptional case is $\mathbf{5}^{+\bullet}$, with a *tert*-butyl group, where such a transformation is much slower. In a previous communication,[16] we explained this fact by the steric effect of the *tert*-butyl group reducing the stabilizing interaction between the diazo and phenyl groups. However, our recent detailed study seems to reveal that the selection of electronic structures is much more complicated than this simple explanation.[39]

The structural changes caused by one-electron oxidations have been documented,[40] but the present case seems to be the only clear-cut example of a turnover of energy levels between HOMO and LUMO.

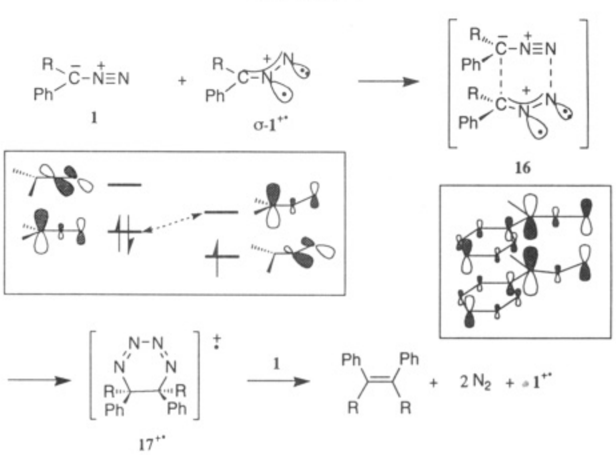
Reaction Mechanism. Important points for the present C–C couplings by the one-electron oxidation of phenyldiazomethanes are summarized as (i) *cis*-stilbenes were preferentially obtained via a chain mechanism, (ii) the C–C coupling reaction was significantly retarded by steric effect, (iii) σ-radical cations were observed by ESR at low temperature, and (iv) π-radical cations with much longer lifetimes were observed from **5** that did not undergo C–C coupling.

It is apparent that a carbenoid mechanism is not likely since the C–C coupling reaction proceeds similarly with various oxidation methods, e.g., the anodic oxidation and the photochemical one-electron transfer. Based on the ESR study (points iii and iv), the most probable intermediate is diazoalkane σ-radical cations. Only σ-radical cations were detected from the diazomethanes, affording stilbenes, and their stability is rationalized by theoretical calculations as described in the previous section. All the important points described above could be explained by the intervention of σ-radicals as discussed in the following.

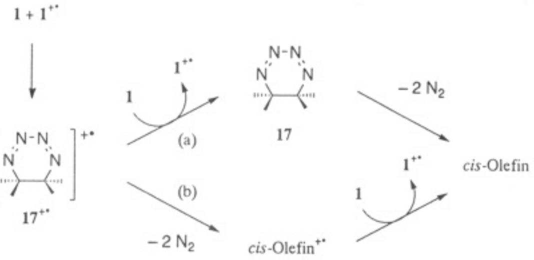
The present C–C coupling reaction is well undertood by a mechanism involving a concerted [4 + 2] cycloaddition between phenyldiazomethane (**1**) and σ-$\mathbf{1}^{+\bullet}$. This formulation is reasonable since diazoalkanes, a typical 1,3-dipolar species, are known to react with dipolarophiles (e.g., electron-deficient olefins)[41] and since the σ-radical cation with only two electrons on the C–N–N allylic π-orbital is expected to behave as a dienophile as in the case of allyl cations.[42]

The frontier molecular orbital theory[43] states that an ideal situation for orbital interaction between two molecules is achieved when interacting HOMO and LUMO orbitals are identical or close to each other. This situation may be realized in the present case between **1**-HOMO and σ-$\mathbf{1}^{+\bullet}$, their orbital shapes being almost identical. A *face-to-face* interaction is favored to achieve a $[_{\pi}4_s + {}_{\pi}2_s]$ cycloaddition as shown in Scheme II. The preferential formation for *cis*-olefins is well explained by the transition state **16** for the cycloaddition; the overlap between the two phenyl groups is expected to stabilize **16** by a secondary orbital interaction similar to the known endo selectivity in Diels–Alder reactions. The observed steric retardation for the olefin formation is also explained by the transition state **16**. When R is Et or Ph in **1**, the transition state should become significantly unstable because of the steric repulsion between the two R groups, leading to no observation of C–C coupling. The steric effect between R = H and R = Et is intermediate and hence the cross olefins may be obtained to some extent as observed.

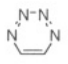
Scheme II

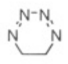


Scheme III



The following steps after the formation of 5,6-dihydro-1,2,3,4-tetrazine **17** are either an electron transfer from **1** to $\mathbf{17}^{+\bullet}$ (pathway a in Scheme III) or a cycloreversion of $\mathbf{17}^{+\bullet}$ to yield *cis*-olefin radical cation (pathway b). As a related species, 1,2,3,4-tetrazines (**18**) are known to be quite unstable[44] owing to a bond-to-bond delocalization of electrons[45] and have been isolated only recently.[46] No 5,6-dihydro-1,2,3,4-tetrazines (**19**) have been prepared.[44] We attempted but failed to detect such intermediates by NMR in the oxidation of **1a** at −50 °C. Of course, this experiment does not deny pathway a involving intermediate **17**.


18


19

In a preliminary report[15] pathway b via *cis*-olefin cation radicals was eliminated because the isomerization of *cis*-stilbene cation radical to the trans isomer was reported to be quite fast.[47] However, several groups have recently

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(39) The dynamics between the π- and σ-radical cations are being studied vigorously. Preliminary results are reported.[14]

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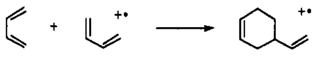
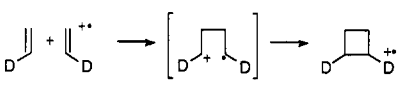
demonstrated that the *cis*-stilbene radical cation is relatively stable, its isomerization rate being smaller than 10^4 s^{-1}.[48] This result indicates that the *cis*-stilbene radical cation would not isomerize to the trans isomer if [**1a**] > 10^{-6} M and the electron transfer from **1a** to the cis cation is expected to be close to the diffusion-controlled rate.[49] Thus, the choice of pathway a or b is not straightforward at present.

Finally, a comparison with other reported cases of pericyclic reactions via radical cations is discussed. Most interesting in the present C–C formation is that a *forbidden* [4 + 4] cyclodimerization of 1,3-dipolar species is turned into an *allowed* [4 + 2] process by one-electron removal. Such a reversal of selectivity is quite contrasted with a hole-catalyzed [4 + 1] cycloaddition of dienes yielding only the Diels–Alder adduct (eq 7),[50] where the thermally *allowed* reaction is accelerated by one-electron oxidation. A [2 + 1] cycloaddition of olefins with the radical cations is known, but it is a stepwise cyclization via 1,4-radical cation intermediates (eq 8).[51] Thus, a turnover of SOMO from π- to σ-orbital for the diazoalkane radical cations brings about the novel cycloaddition as shown in Scheme II.



(7)



(8)

Conclusion. One-electron oxidation of phenyldiazomethanes affords *cis*-stilbenes predominantly. This C–C coupling is shown to proceed via a chain reaction involving diazomethane radical cations. It is shown by ESR that one-electron removal from the HOMO π-orbital yields σ-radical cations with a turnover of HOMO and LUMO. This novel turnover and [4 + 2] cycloaddition are rationalized on the basis of theoretical calculation for the radical cations.

Experimental Section

^{1}H NMR spectra were recorded with Hitachi R24B (60 MHz), Varian XL-GEM-200 (200 MHz), and JEOL GX-400 (400 MHz) NMR spectrometers. GLC analyses were performed with a Yanagimoto G180 gas chromatograph, using 2.5-mm × 1-m column of Carbowax 300 M (2%) on Chromosorb WAW. Shimadzu Chromatopac C-R1B and C-R3A integrators were used for quantitative analyses. GC-MS analyses were carried out with a JEOL D300 mass spectrometer using a 2.5-mm × 1-m column of Ultrabond PEGS (Gasukuro Kogyo inc.). Absorption spectra were recorded on a Hitachi ultraviolet spectrometer (Model 124).

Materials. Dichloromethane and acetonitrile were dried over CaH_2. 9,10-Dicyanoanthracene (DCA)[52] and tris(*p*-bromophenyl)aminium hexachloroantimonate[53] were prepared according to the published procedures. Copper(II) perchlorate was dehydrated as described by Bethell et al.[3] Phenyldiazomethanes (**1a–e**, **4**, and **5**)[54] and diphenyldiazomethane (**6**)[55] were synthesized and purified by the reported procedures. The purities of diazomethanes were over 95% as determined by ^{1}H NMR.

Aryl-*tert*-butyldiazomethanes 5a–c. Pivalophenone and its *p*-methyl and *p*-methoxy derivatives were prepared by known methods.[56] Hydrazones of the pivalophenones were obtained quantitatively from the ketones (1.0 g) following 8 h of reflux in EtOH (20 ml) with hydrazine hydrate (10 mL). A mixture of the hydrazones (0.5 g), yellow mercuric oxide (2.0 g), anhydrous sodium sulfate (1.0 g), and 0.1 mL of saturated KOH–EtOH solution in 20 mL of ether was stirred vigorously at room temperature for 2 h. The reaction mixture was filtered and solvent was evaporated from the filtrate under reduced pressure. Aryl-*tert*-butyldiazomethanes were obtained quantitatively.

Phenyl-*tert*-butyldiazomethane (5a): orange oil; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9 H), 6.9–7.4 (m, 5 H).

(*p*-Methylphenyl)*tert*-butyldiazomethane (5b): orange oil; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9 H) 2.28 (s, 3 H) 7.00 (s, 4 H).

(*p*-Methoxyphenyl)*tert*-butyldiazomethane (5c): red oil; ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 9 H) 3.68 (s, 3 H) 6.80 (d, J = 9.0 Hz, 2 H), 7.00 (d, J = 9.0 Hz, 2 H).

1,6-Bis(diazo)-1,6-diphenylhexane (7). 1,6-Diphenyl-1,6-hexanedione dihydrazone was obtained following 12 h of reflux of the corresponding diketone[57] (2.0 g) in ethanol (20 mL) with hydrazine hydrate (20 mL): mp 105–118 °C; ^{1}H NMR ($CDCl_3$) δ 1.55 (m, 4 H) 2.53 (m, 4 H) 5.35 (bs, 4 H) 7.0–7.6 (m, 10 H). A mixture of the dihydrazone (1.0 g), yellow mercuric oxide (5.0 g), anhydrous sodium sulfate (5.0 g), and 0.1 mL of saturated KOH–EtOH solution in 50 mL of ether was stirred vigorously at room temperature for 6 h. The reaction mixture was filtered and solvent was evaporated from the filtrate under reduced pressure. The bis(diazo) compound was obtained quantitatively: ^{1}H NMR ($CDCl_3$) δ 1.70 (m, 4 H) 1.48 (m, 4 H) 6.7–7.4 (m, 10 H).

Cyclic Voltammetry. The oxidation peak potentials (E_p^{ox}) of diazoalkanes were measured by cyclic voltammetry in acetonitrile containing 0.1 M $LiClO_4$ using a Yanagimoto polarographic analyzer P-1100. Glassy carbon electrode, platinum wire, and Ag/AgCl were used as working, counter, and reference electrodes, respectively. E_p^{ox} of **1a** observed with 100 mV/s scan rate at room temperature is +0.94 V, and those of other diazoalkanes are shown in Table II.

DCA-Sensitized Photooxidation of Phenyldiazomethanes. Typically, a 3-mL acetonitrile solution of 3 mM phenyldiazomethane (**1a**) and 0.4 mM DCA in a 24-mL Pyrex tube with a rubber septum was purged with argon for 10 min and irradiated with a 300-W medium pressure Hg lamp through a 5% $NaNO_2$ filter solution (i.e., >400 nm) at ca. 20 °C. The orange color of **1a** faded completely by the irradiation for 1.5 h. Products were identified by GC-MS analysis in comparison to authentic samples and their yields were determined by GLC. The photooxidation of **1b** proceeded similarly, but **1c**, **1d**, and **1e** were oxidized much more slowly and were not completely by prolonged irradiation of 5 h. For these cases, the remaining diazoalkanes were quenched by acetic acid and products were determined by GLC. On the other hand, the photooxidation under an oxygen atmosphere was quite fast and completed within 10 min, affording the benzaldehydes quantitatively.

Electrochemical Oxidation of Phenyldiazomethanes. Electrolysis was performed using a Hokuto Denko HP300 potentiostat in a 3-cm-diameter Pyrex vessel capped with a rubber stopper, two 1-cm × 3-cm platinum plates as working and counter electrodes, and a Ag/AgCl reference electrode. A 10-mL acetonitrile solution of 45 mM **1a** and 0.1 M lithium perchlorate was purged with argon and electrolyzed at +1.2 V vs Ag/AgCl until the color of **1a** disappeared; the products were determined similarly. The current efficiency was obtained from a coulometric analysis during ca. 10% conversion of **1a** as monitored by absorption spectroscopy (**1a**; λ_{max} = 485 nm, ϵ = 36).

Chemical Oxidation of Phenyldiazomethanes. A 3-mL acetonitrile solution of 10 mM phenyldiazomethane (**1a**) in a

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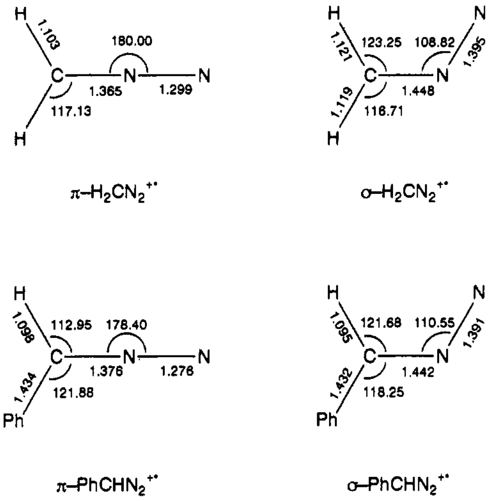

Figure 4. Optimized geometries for $H_2CN_2^{+•}$ and $PhCHN_2^{+•}$ calculated by UHF/STO-3G.

24-mL test tube with a rubber septum was purged with argon, and then a 0.1-mL acetonitrile solution of 4.5 mM copper(II) perchlorate was added using a syringe. The solution became colorless within 1 min, and the products were determined similarly by GLC. Oxidation with a tris(*p*-bromophenyl)aminium hexachloroantimonate (6.6 mM) solution was carried out in the same way.

Formation of 1,2-Diphenylcyclohexene (8) from Bis(diazo) Compound 7. An acetonitrile solution of 2.0 mM 7 and 0.2 mM DCA was purged with argon and irradiated (>400 nm) for 5 min. The product 8 was identified by ^1H NMR and by GC-MS in comparison to the authentic sample,[58] and the yield determined by GLC was 96%. Similarly, the oxidation of 2.0 mM 7 by copper(II) perchlorate (0.03 equiv) afforded 8 in 95% yield.

ESR Measurement. ESR spectra were measured on a Varian E-112/V7800 spectrometer equipped with a temperature controller. The microwave frequency was measured with a Takeda Riken 5201M frequency counter, and the resonance magnetic field values of the signals were measured with the aid of a Varian E500 NMR G-meter.

A simple two-electrode cell for low-temperature ESR studies developed by Ohya-Nishiguchi[59] was employed. The sample solution was degassed in the reservoir of the cell by repeated freeze–pump–thaw cycles and poured into the quartz tube. No reference electrode was used in the ESR measurements, but the applied potential vs Ag/AgCl could be calibrated from the applied voltage using a Hokuto Denko HA301 potentiostat. The sample was cooled in ESR the cavity and the applied voltage was raised. The ESR spectra were recorded at optimal voltage on steady state.

Theoretical Calculations. The calculations were carried out on FACOM M-780/20 or HITAC M-680H and S-820/80 computers using GAUSSIAN 80[60] or GAUSSIAN 82[61] programs. The structures of π- and σ-$PhCHN_2^{+•}$ were optimized with the UHF/STO-3G[33] procedure, and using the geometry the energies were recalculated with MP2/STO-3G.[34] Both the structures have energy minima in planer C_s symmetry, and the bond lengths and angles are summarized in Figure 4.

The spin densities of σ-$H_2CN_2^{+•}$ and $H_2C{=}N{-}O^•$ were calculated with the UHF/4-31G procedure.[37] The optimized geometries and total energies for σ-$H_2CN_2^{+•}$ are as follows: bond lengths, R(C–N) = 1.350 Å, R(N–N) = 1.208 Å, $R(C–H_{syn})$ = 1.079 Å, $R(C–H_{anti})$ = 1.073 Å; bond angles, C–N–N = 124.07°, H_{syn}–C–N = 122.21°, H_{anti}–C–N = 116.59°; total energy, −147.245559 au. For $H_2C{=}N{-}O^•$: bond lengths, R(C–N) = 1.288 Å, R(N–O) = 1.289 Å, $R(C–H_{syn})$ = 1.071 Å, $R(C–H_{anti})$ = 1.066 Å; bond angles, C–N–O = 124.21°, H_{syn}–C–N = 122.65°, H_{anti}–C–N = 117.15°; total energy, −167.984856 au.

Acknowledgment. We acknowledge Prof. Hiizu Iwamura, Prof. Tadashi Sugawara, and Dr. Akira Izuoka for their helpful discussion. Thanks are due to the Instrument Center, the Institute for Molecular Science (IMS), for assistance in obtaining the ESR spectra. This work was supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Science and Culture. The numerical calculations have been carried out at IMS Computer Center and Nagoya University Computer Center.

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Salt Effects on Supramolecular Complexation and Catalysis[1]

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Received October 1, 1991

Complexation equilibria between a positively charged azoniacyclophane (CP66) and naphthalene-2-carboxylate in water show a linear Debye–Hückel correlation with a sensitivity of $m = -1.5$ compared to the $m = -4.1$ for pure ionic complexes observed experimentally and predicted theoretically. The m values can be used as a scale for ionic vs lipophilic van der Waals binding contributions; the latter dominate in the present azoniacyclophane complexes. Complexation-induced NMR shifts (CIS) vary from −0.3 ppm to −1.6 ppm shielding and demonstrate in all cases intracavity inclusion with different geometries. The cyclophane CP66 enhances rates of nucleophilic substitution of 1-chloro-2,6-dinitrobenzoic acid (2) with OH^- by a factor of up to ~2, with NO_2^- by up to ~8. The elimination from 2-(*p*-nitrophenyl)ethyl mesylate to *p*-nitrostyrene under basic conditions is enhanced by up to ~5; the saturation curve obtained in this case indicates a limiting $k_{cat}/k_{un} \cong 10$ and a binary complex constant of $K \approx 15\ M^{-1}$. Salt effect studies show that a considerable part of the rate enhancements by macrocyclic polyammonium ions can be due to the increase of ionic strength as a consequence of the multiple charges in the catalyst. The ionic strength/salt effect contribution is large in the reaction of 2 with OH^-, but smaller for the other two reactions.

The presence of salts can have a profound effect on the complexation between organic host and guest molecules,[2] as well as on their catalytic properties. This is expected especially for interactions with host structures bearing

0022-3263/92/1957-3066$03.00/0