bonate solution. The crude product was recrystallized from chloroform to yield 1.2 g of yellow crystals. mp. 288-289℃ (dec.). IR (KBr) 3490 cm^{-1} (OH), 1725 cm^{-1} (-COO-), 1520 and 1340 cm^{-1} ($-NO_2$). ^{1}H-NMR ($CDCl_3$) δ 7.99 (s, 4H, ArH with nitro group), 7.0-8.3 (m, 16H, ArH), 3.6-4.2 (pair of d, 8H, ArCH$_2$Ar).

5,17-Dinitro-25,26,27,28-tetrahydroxycalix[4]arene 7. To a solution of 0.72 g of 6 in 50 m*l* of THF, 15 m*l* of water, and 30 m*l* fo EtOH, 2.48 g of NaOH was added and refluxed for 15 h. Solvents were removed under reduced pressure and the residue was acidified with 2N HCl.

Precipitate was collected and washed with MeOH.

Recrystallization from chloroform-MeOH yields 0.3 g of gray crystals. mp. 296-298℃ (dec.). IR (KBr) 3210 cm^{-1} (OH), 1520 and 1330 cm^{-1} (-NO$_2$). ^{1}H-NMR (DMSO-d$_6$) δ 9.82 (br s, 4H, OH), 8.05 (s, 4H, ArH containing nitro groups), 7.13 (d, 4H, ArH, *J*=7.5 Hz), 6.62 (t, 2H, ArH, *J*=7.5 Hz), 3.94 (br s, 8H, ArCH$_2$Ar). ^{13}C-NMR (DMSO-d$_6$) δ 161.44, 150.40, 138.26, 130.19, 128.73, 128.40, 124.09, and 120.53 (Ar), 30.77 (-CH$_2$-).

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Photodecomposition Mechanism of Diazoindanones by Laser Photolysis and Lamp Photolysis

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The mechanism for the photodecomposition reactions of 2-diazoindan-1-one and 1,3-bis(diazo)indan-2-one have been studied in benzene, toluene, methanol, cyclohexane and acetonitrile solvents using laser photolysis and lamp photolysis. A triplet ketocarbene is observed from the photolysis of bis diazo compounds by the loss of nitrogen molecule from the carbene precursors. It is concluded that the Wolff rearrangement, which involves the formation of a ketene intermediate, can be regarded as a concerted process in nanosecond time scale. The photolytic reactions of diazoindanones in methanol give Wolff rearrangement products, but those in benzene do not involve in the Wolff rearrangement.

Introduction

The photochemical extrusion reaction of aromatic α-diazo ketones into the corresponding aromatic carboxylic acid *via* the Wolff rearrangement has been widely studied by photoresist methods[1]. The Wolff rearrangement in those photodecomposition reactions proceeds through an intermediate ketene. It is well known that the phototransformation of 2-diazo-1,2-naphthoquinones gives a product of 3-indenecarbo-

xylic acid, where the photodecomposition produces an intermediate ketene[2]. It has been suggested that, in some cases, a long-lived intermediate ketene absorb another photon, leading to the photoresist chemistry.

Generally, the conversion of aromatic α-diazo ketones into aromatic ketenes involves an 1,2-migration of a carbon atom, which is known as the Wolff rearrangement. Despite many investigations, the mechanism involving aromatic bis (diazo) ketone and diazo indanone is yet uncertain. That is, it is not clear in those reactions whether a concerted process occurs at the step of the loss of nitrogen or at the step of simultaneous migration of the 1,2-carbon atoms. The other

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point of dispute in the Wolff rearrangement of diazo aromatic and indanone compounds is that whether the reaction proceeds through a two-step process which produces an α-keto carbene or an oxirane-like intermediate. The present investigation is undertaken in an attempt to investigate the mechanism regarding the Wolff-rearrangement. Thus, the transient absorption and the fluorescent emission measurements have been applied to the photodecomposition mechanism of 2-diazoindan-1-one and 1,3-bis(diazo)indan-2-one in various solvents. We also carried out the photolytic reaction of diazoindanones in methanol and benzene under the condition of the low intensity light irradiation (high pressure mercury lamp).

Experimental

Materials. 2-Diazoindan-1-one (DIN-1) and 1,3-bis(diazo) indan-2-one (BDIN-2) were synthesized by the reaction of the corresponding aromatic oximino ketone following the methods of Cava[3], Trost[4] and Foster[5]. Isoamylinitrite was added dropwise to an ether solution of 1-indanone or 2-indanone at −10℃. After the reaction was completed, 1,3-bis (oximino)indan-2-one and 2-oximinoindan-1-one were isolated by suction filtration using a rotary evaporator followed by vacuum drying.

1,3-Bis(diazo)indan-2-one(BDIN-2). 10 m*l* of 1N-NaOH solution was added dropwise while stirring into a three-necked flask. The flask was equipped with a magnetic stirrer, a nitrogen inlet, and an additional funnel, that contains a solution of 0.5 g of 1,3-bis(oximino)indan-2-one in 10 m*l* of H_2O cooled in an ice bath. 10 m*l* of 15N-NH_4OH solution was added dropwise to the mixture.

After the addition was completed, 30 m*l* of 5%-NaOCl solution was added dropwise slowly to the mixture. The reaction mixture was stirred in the cold bath for 1.5 hours and was then allowed to stand at room temperature overnight under nitrogen. The following day, the red black precipitate in the reaction mixture was dissolved in 50 m*l* of $CHCl_3$ and washed with water. Two liquid layers were present. The $CHCl_3$-layer, a reddish solution, was dried over $MgSO_4$ anhydride and was rotary-evaporated, and was dried over vacuum. The red solid weighted 0.3 g, corresponding to a 62% yield; mp. 126-127℃ ; IR (KBr), 2100, 2080, 1645, 1390, 1180, 1090 cm^{-1} ^{1}H-NMR (CDCl$_3$) δ 7.2 (s, 4H)

2-Diazoindan-1-one(DIN-1). The diazo compound was similarly prepared by substituting 2-oximinoindan-1-one for 1,3-bis(oximino)indan-2-one. This product (68% after recrystallization from ether/petroleum ether) was red brown solid; mp. 110-112℃ ; IR (KBr), 2080, 1600-1680, 1460, 1380, 1180, 1160, 930 cm^{-1}, ^{1}H-NMR (CDCl$_3$) δ 7.2 (s, 4H), 1.9-2.1 (m, 1H), 2.6 (d, 1H).

Benzene, toluene, methanol, cyclohexane and acetonitrile were purified by the methods[6] suggested in the appropriate spectroscopy literature.

Apparatus. Proton magnetic resonance (^{1}H-NMR) spectra were recorded on a Varian XL 400 spectrometer or a Bruker FT-300 MHz Aspect-3000 spectrometer in deuteriochloroform (unless otherwise noted) with tetramethylsilane as an internal standard. GC/MS analysis was performed using a Hewlett-Packard 5996 system. Infrared absorption (IR) spectra were recorded on a Perkin-Elmer Model 683

grating spectrophotometer. UV-absorption spectra were obtained on a UVIKON 940 spectrophotometer.

An irradiation cell (10×10 mm, 3 m*l* Suprasil quartz cuvette) was connected with Teflon tubings to a reservoir where the solutions were deaerated by bubbling with oxygen-free nitrogen. Transient absorption data were recorded by excitation with LEXtra-50 excimer laser delivering 80 mJ/pulse at 308 nm of 5 ns pulse width by the gas mixture of Xe-HCl. This beam was incident on the sample at 90° with respect to the monitoring beam. A xenon lamp provides the analyzing light to monitor the changes in the optical density. Special care was taken in aligning the system so that the two beams overlap within the same volume of sample. A digital delay was introduced in 5-ns steps in order to achieve the proper sequence of triggering of the detection system at any point of the photolysis.

Photodecomposition Product. A solution (20-30 m*l*) of the diazo compound (50-80 mg) in each solvent was placed in a "merry-go-round" apparatus, purged with argon for 10 minutes, and irradiated with a 300 W high-pressure mercury lamp at room temperature. The photodecomposition products were isolated by solvent evaporation under reduced pressure at room temperature. The isolates were characterized by GC/MS and ^{1}H-NMR.

Preparative Irradiation by High Pressure Mercury Lamp

Irradiation of BDIN-2 in Methanol. A solution of 30 mg of BDIN-2 in 15 m*l* of methanol was irradiated with 300 W high-pressure mercury lamp for 3 hours. The ^{1}H-NMR spectrum of the reaction mixture showed the characteristic peaks due exclusively to methyl *o*-(dimethoxymethyl)phenylacetate. The yield of methyl *o*-(dimethoxymethyl)phenylacetate was estimated to be 67%, by GC: colorless oil; ^{1}H-NMR (CDCl$_3$) δ 3.30 (6H, s), 3.67 (3H, s), 3.78 (2H, s), 5.46 (1H, s), 7.0-7.5 (4H, m); IR (neat) 1740 cm^{-1}; CG/MS m/z (relative abundance) 209 (M^{+}-Me, 4), 193 (M^{+}-OMe, 66), 161 (100), 151 (57). A solution of 30 mg of BDIN-2 in 15 m*l* of methanol was irradiated for 1 hour. After evaporation of the solvent under reduced pressure, the residue was separated by HPLC with chloroform as eluent. 4 mg of 1-diazo-3-methoxyindan-2-one was obtained. 1-Diazo-3-methoxyindan-2-one: orange oil; ^{1}H-NMR (CDCl$_3$) δ 3.56 (3H, s), 4.80 (1H, s), 7.11 (1H, d, *J*=7.1 Hz), 7.20 (1H, dd, *J*=7.1, 7.1 Hz), 7.3-7.5 (2H, m); IR (neat) 2090, 1695 cm^{-1}.

Irradiation of BDIN-2 in Benzene. A solution of 30 mg of BDIN-2 in 15 m*l* of dry benzene was irradiated for 5 hours. After evaporation of the solvent, the residue was separated by HPLC with chloroform as eluent to give two products: dispiro[indan-1,7'-norcara-2',4'-diene-3,7"-norcara-2",4"-dien]-2-one (48% yield): colorless needles; mp. 154-155 ℃ ; ^{1}H-NMR (CDC$_3$) δ 3.19 (4H, m), 6.10 (4H, m), 6.49 (4H, m), 6.79 (2H, m), 7.08 (2H, m); IR (KBr) 1700 cm^{-1}; GC/MS m/z (relative abundance) 284 (M^{-}, 7), 256 (M^{+}-CO, 60), 178 (M^{+}-C$_6$H$_6$-CO, 100); 3-diazospiro[indan-1,7'-norcara-2',4'-dien]-2-one (39% yield); orange needles; mp. 140-141℃ ; ^{1}H-NMR (CDCl$_3$ δ 3.23 (2H, m), 6.10 (2H, m), 6.50 (2H, m), 6.73 (1H, d, *J*=7.7 Hz), 7.02 (1H, dd), 7.76 (1H, d), 7.26 (1H, dd); IR (KBr) 2080, 1680 cm^{-1}; GC/MS m/z (relative abundance) 206 (M^{+}-N$_2$, 38), 178 (M^{+}-CO-N$_2$, 62), 128 (M^{+}-C$_6$H$_6$-CO, 100)
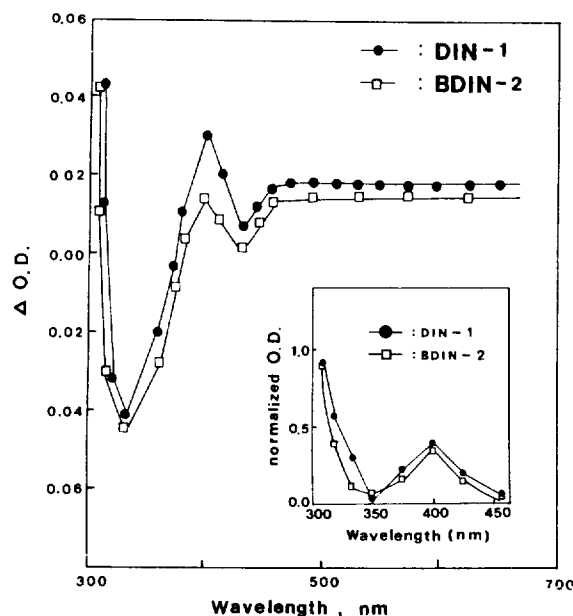
Irradiation of DIN-1 in Methanol. A solution of 30
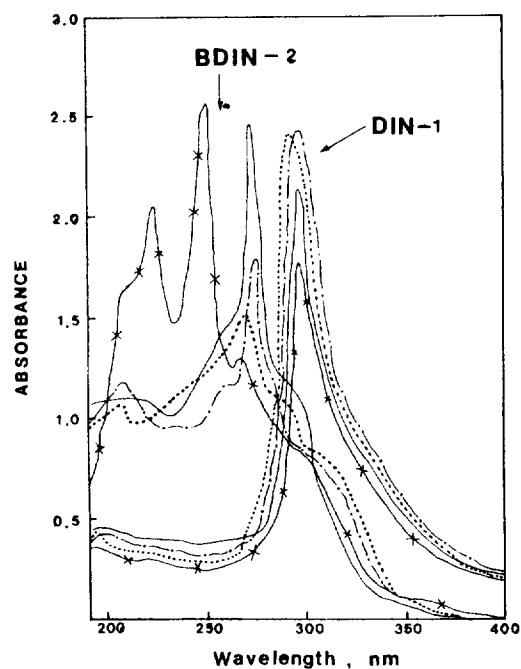
Figure 1. The aborption spectra of DIN-1 and BDIN-2 in benzene (—), toluene (—·—), cyclohexane (·····) and acetonitrile (−×−), respectively.

Figure 2. Transient absorption spectra of DIN-1 and BDIN-2 in acetonitrile after 308 nm laser pulse excitation to zero; Inset: Calculated absorption spectra (normalized at 350 nm).

mg of DIN-1 in 15 ml of dry methanol was irradiated for 3 hours. After evaporation of the solvent, the residue was separated by HPLC with chloroform as eluent to give 2-methoxyindan-1-one (68% yield) and methyl o-methoxymethylphenylacetate (12% yield): 2-methoxyindan-1-one; mp. 105-107℃ ; ¹H-NMR (CDCl₃) δ 3.25 (2H, s), 3.73 (3H, s), 7.85-7.99 (4H, m); IR (KBr) 1696, 1602, 1493, 1308, 1254, 1096 cm⁻¹; GC/MS m/z (relative abundance) 162 (M⁺, 6), 131 (M⁺-OCH₃, 72), 103 (M⁺-OCH₃-CO, 100). Methyl o-methoxymethylphenylacetate; Colorless oil; ¹H-NMR (CDCl₃) δ 3.42 (3H, s), 3.68 (3H, s), 3.79 (2H, s), 5.51 (2H, s), 7.2-7.6 (4H, m); IR (KBr) 1738 cm⁻¹, GC/MS m/z (relative abundance 194 (M⁺, 8), 163 (M⁺-OCH₃, 67), 104 (M⁺-OCH₃-CO₂CH₃, 100)
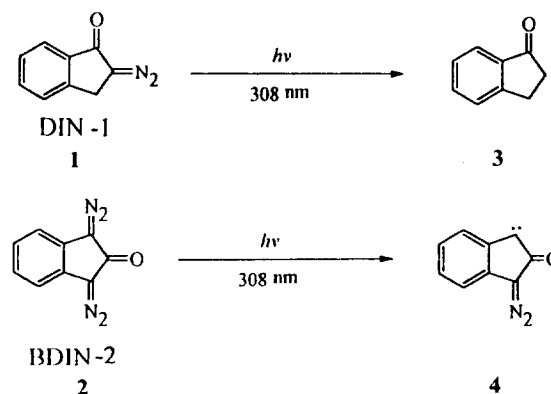
Irradiation of DIN-1 in Benzene. A solution of 30 mg of DIN-1 in 15 ml of dry benzene was irradiated for 3 hours. After evaporation of the solvent, the residue was separated by a TLC plate to give spiro[indan-1,7′-norcara-2′,4′-dien]-1-one spiro[indan-1,7′-norcara-2′,4′-dien]-1-one (64% yield); yellow needles; mp. 138-142℃ ; ¹H-NMR (CDCl₃) δ 3.04 (2H, m), 3.25 (2H, m), 6.13 (2H, m), 6.51 (2H, s), 7.02-7.18 (3H, m), 7.24 (1H, dd); IR (KBr) 2060, 1690 cm⁻¹; GC/MS m/z (relative abundance) 208 (M⁻, 38), 130 (M⁺-C₆H₆, 42), 102 (M⁻-C₆H₆-CO, 100).

Results and Discussion

Transient Absorption and Fluorescence Spectra of Carbenes. Figure 1 shows the absorption spectra of DIN-1 and BDIN-2 in various solvents. As shown in Figure 1, the absorption bands of the diazo compounds of DIN-1 and BDIN-2 were observed in the UV region, 210-350 nm as stable species at low intensity of UV light. Usually the transient absorption spectra[7] are used for measuring the differe-

Scheme 1.

nce of absorption between the transient species and its stable precursor. Transient absorption spectra of carbenes are represented as the changes of optical density in laser photolysis experiments. Figure 2 represents the transient absorption spectra recorded at 250 ns delay after 308 nm laser excitation of DIN-1 and BDIN-2 in acetonitrile. The bleaching around 330 nm agrees well with the absorption by the ground state carbene[8]. The laser excitation at 308 nm generates diazo keto carbene in the case of BDIN-2, and ketocarbene in the case of DIN-1, respectively as shown in Scheme 1.

In addition to the bleaching peak around 330 nm, there exists an absorption that shows not-well defined maximum in the wavelength region below 330 nm. It should be noted that the laser photolysis leads to an absorption difference (ΔOD) rather than an absolute spectrum. Thus, in order to estimate the net absorption changes induced by the transient species, it was assumed that carbene species do not absorb at 350 nm (the wavelength at which maximum bleaching peak is normalized to zero).
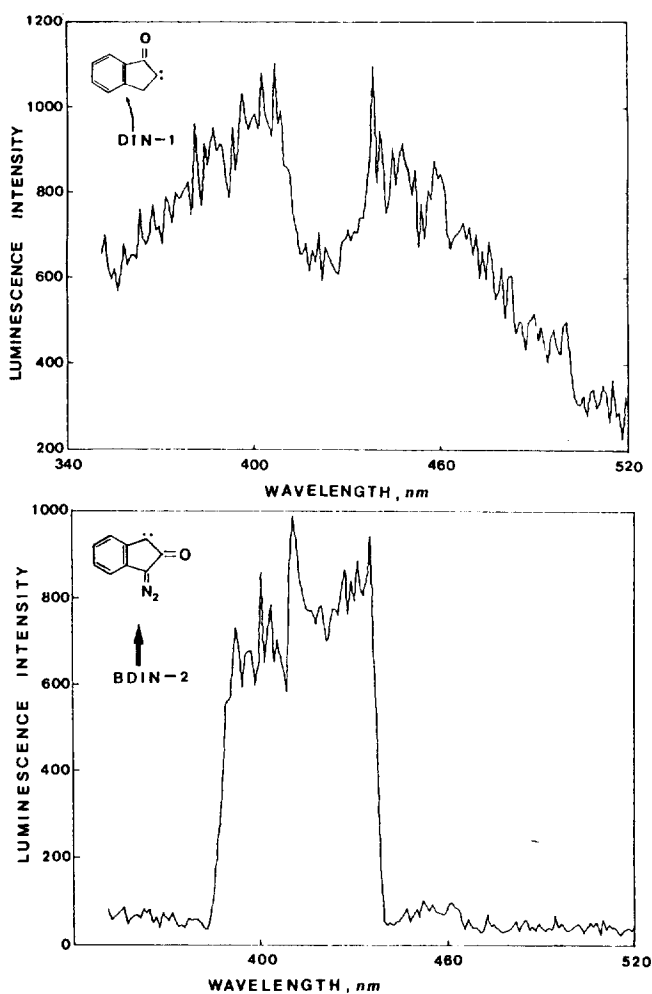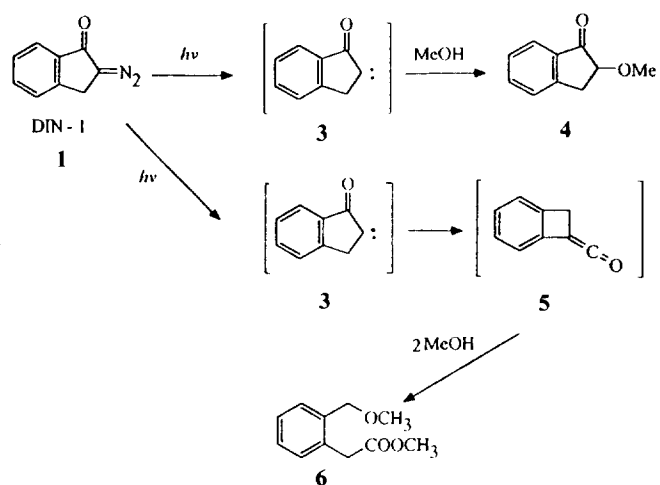
Figure 3. Fluorescence spectra of the excited carbenes monitored after excitation of the carbenes produced from DIN-1 and BDIN-2 in acetonitrile. The carbenes were prepared by 308 nm decomposition of DIN-1 and BDIN-2.
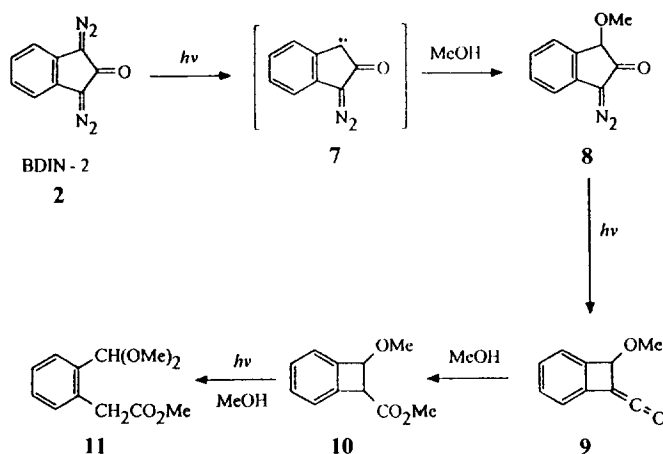

Scheme 2.

Scheme 3.

A calculated spectrum due to the transient species was obtained from the absorption difference (ΔOD) observed and the known ground state absorption spectrum of the original solution. The substraction at each wavelength leads to an absorption spectrum having an absorption band centered at *ca.* 400 nm and another more intense band below 320 nm. Nevertheless, this approach is suitable to obtain the approximate spectra for carbene transient, but inappropriate to search for mechanistic evidences. The transient absorption spectra in Figure 2 are in accordance with those of the other excited state carbenes produced under the photochemical condition[9].

The fluorescence spectra of carbenes are shown in Figure 3. The spectra were obtained in acetonitrile with 308 nm pulse excitation. A strong fluorescence is observed at 438 nm in DIN-1 and at 436 nm BDIN-2, respectively. The excitation of a degassed acetonitrile solution containing DIN-1 or BDIN-2 ($\sim 10^{-3}$ M) with 308 nm pulses leads to N_2 extrusion from the excited precursor, thereby producing the carbene.

Photoreaction Product Analyses of Diazoindanones in Methanol and Benzene. In order to obtain more information on the nature of the unidentified transient, pro-

duct analyses of photoreaction of DIN-1 and BDIN-2 in methanol and benzene were carried out after continuous irradiation by a high-pressure mercury lamp. The reaction mixture in methanol was separated by HPLC with chloroform eluent, yielding 2-methoxyindan-1-one (**4**) and methyl-*o*-methoxymethylphenylacetate (**6**) in 68% and 12% yield, respectively.
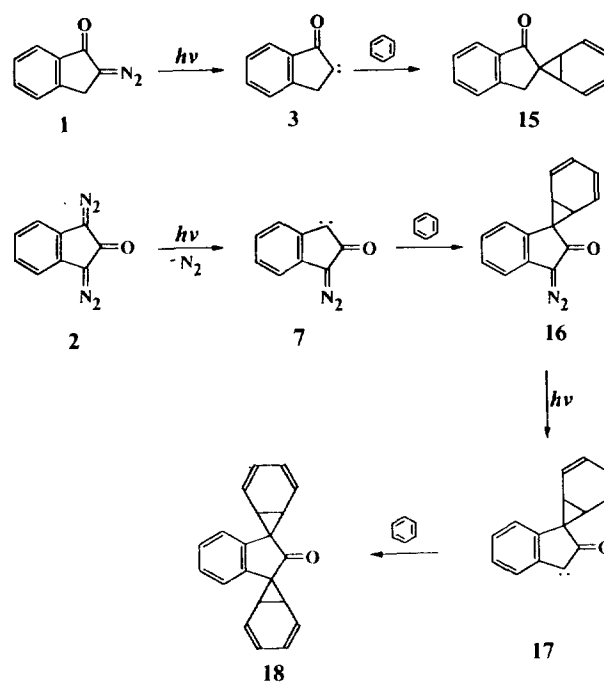
Irradiation of DIN-1 gives ketocarbene (**3**), which is captured by methanol to afford the 2-methoxyindan-1-one (**4**). Another route shows that the ketocarbene (**3**) gives a ketene (**5**), which could be formed by a Wolff-type rearrangement of ketocarbene and finally produces methyl-*o*-methoxymethylphenylacetate (**6**). Irradiation of BDIN-2 in methanol by a high-pressure mercury lamp gave about 37% of 1-diazo-3-methoxyindan-2-one (**8**) and about 43% of methyl-*o*-(dimethoxymethyl)phenylacetate (**11**). A possible reaction route from BDIN-2 to the products can be revealed as shown in Scheme 3.

Mono diazo compound (**8**) was obtained in the case of a short-irradiation time of about 1 hour, but a two carbene center inserted product (**11**) was obtained when irradiated for about 3 hours. The results of product analyses of methanol insertion reaction to the carbene suggest that an oxirene-like intermediate (**12** and **13**) is not produced as shown in Scheme 4.

Scheme 4.

Scheme 5.
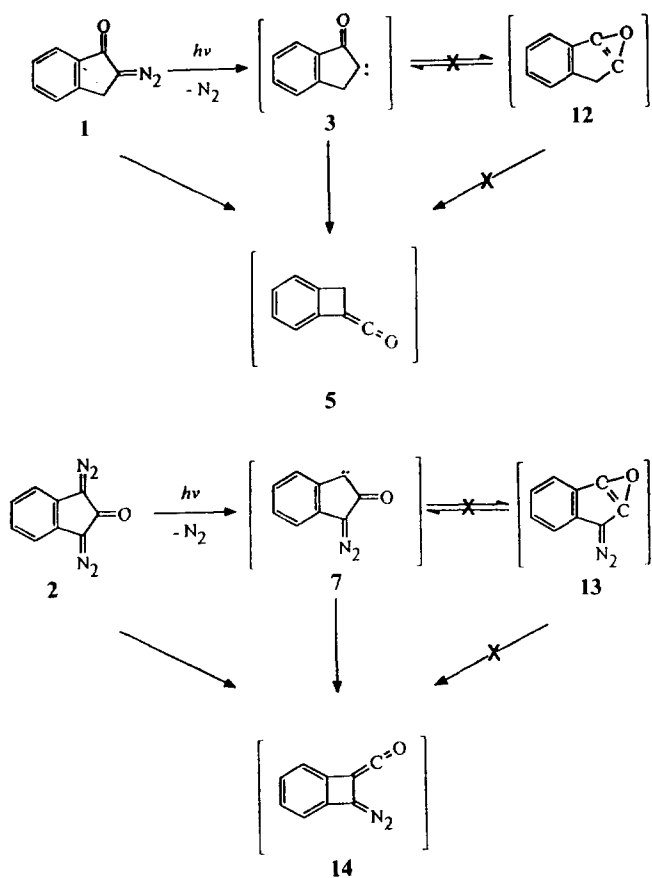
From photolyses of 2-diazo-1,2-naphthoquinones, Tanigaki *et al*[10]. suggests the involvement of two transients; the first is assigned to an oxirene-like intermediate and the second long-lived on to the ketene. Their assignment of the chemical structures was based on the kinetic and the thermodynamic results only.

However, they did not discuss their results in the context of earlier work that ruled out the involvement of oxirene-like intermediates on the basis of labeling experiments[11]. In previous discussion of this work, the transient spectra are similar to the data of the ketene intermediates (5 and 14) which have been reported by Rosenfeld[12]. In the IR spectra of a diazoketone at 77 K, the ketene transient was observed. To find further evidence for the existence of the oxirene-like intermediate, we have tried to trap the oxirenes (12 and 13 in Scheme 4) in solid argon matrix at 10 K several times by means of IR spectroscopy. However, the oxirenes could not be detected by the IR spectrum in the argon matrix. The irradiation of DIN-1 and BDIN-2 by a high pressure mercury lamp in Ar matrix at 10 K showed a C=O stretch band at 1647 cm^{-1}, one of the first formed carbonyl compounds, which was assigned to the ketocarbene (3) and the diazo ketocarbene (7). Our results are consistent with the IR works of Chapman and his co-workers[13]. Continued irradiation in the Ar matrix resulted in the second sharp peak for the ketene intermediate (5) and the diazo ketene intermediate (14) having the intense IR peak at 2106 cm^{-1}. The two ketene intermediates (5 and 14) could be formed by a Wolff-rearrangement from the carbenes (3 and 7). Howe-

ver, we could not find the peak corresponding to oxirenes (12 and 13) from the IR spectrum in the Ar matrix at 10 K.

The irradiation of benzene solution of DIN-1 gave spiro [indan-1,7'-norcara-2',4'-dien]-1-one 15 (42%). And the irradiation of benzene solution of BDIN-2 gave dispiro[indan-1,7' -norcara-2',4'-diene-3,7''-norcara-2'',4''-dien]-2-one 18 (37%) and 3-diazospiro[indan-1,7'-norcara-2',4'-dien]-2-one 16 (29 %), respectively. The reaction routes of the photolytic reaction of DIN-1 and BDIN-2 in benzene are illustrated as in Scheme 5. All these products from the photolytic reaction of DIN-1 and BDIN-2 have been originated from the ketocarbene intermediates (3 and 7), which are not involved in the Wolff rearrangement.

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MO study of Hydride Transfer between NADH and Flavin Nucleotides

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The mechanism has been MO-theoretically described for the reaction of NADH and flavin nucleotides. Their bioactive regions were found to be the part forming transbutadiene type in the molecular by examing the respective HOMO and LUMO electron densities of nicotinamide ring and isoalloxazine ring of flavin. The elecron densities of 1, 2, 3 and 4 positions of the transbutadiene part were found to be considerably larger than those of any other positions in the molecules. A loose molecular complex, which stacks with congruity between C(4) of nicotinamide ring and N(5) of the isoalloxazine ring, was estimated to be formed by calculating the quantities of charge transfer occuring through 1, 2, 3 and 4 positions between them. Accordingly, we propose the mechanism that molecular complex first would be formed and follwed by the hydride transfer.

Introduction

Flavin coenzymes of flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD) are derived coenzymatically from vitamine B_2 riboflavin. They function as tightly bound prosthetic groups of flavoproteins or flavoenzymes. It is well known that the reduction of flavin nucleotides by the reduced nicotinamide adenine dinucleotide (NADH) occurs by the direct hydride transfer.

Hydride (*H⁻) transfers from C(4) of nicotinamide ring to N(5) of isoalloxazine ring of FMN or FAD[1]. Though experimental studies were carried out to explore the above reaction[2], theoritical studies are rarely found[3].

We have shown that the active region of chemical carcinogens is the transbutadiene (TB) part in the molecule[4]. There must exist a corresponding active region for any cellular component to interact with the TB part of chemical carcinogen. Assuming the existence active region of a cellular component, this TB model would be applied to predict the activity of mutagens, toxitants and drugs.

We have confirmed as a matter of fact that active sites of mutagens, toxitants and drugs are all the same 1, 2, 3, and 4 atoms of TB part[8]. An attempt will be made to apply this model to a biochemical reaction of NADH with flavin.

Method and Model
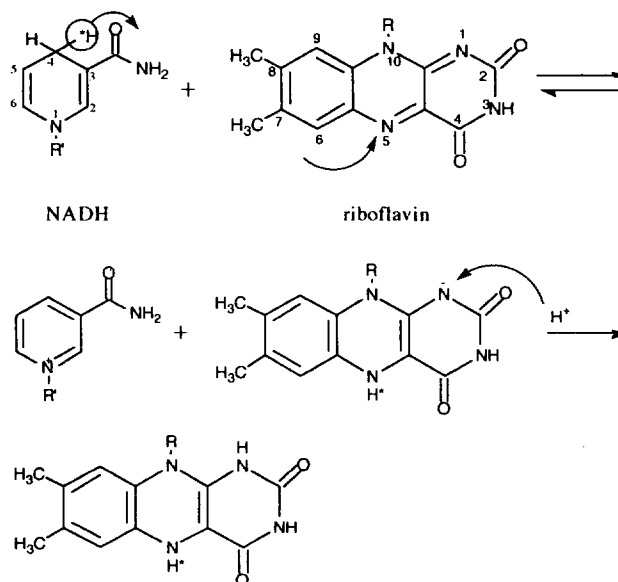
MO molecular orbital calculation was carried out at the

Figure 1. Transfer of reducing equivalents from NADH to flavin.

extended Hückel level for the nicotinamide ring and isoalloxazine ring in which CH_3 group were substitude for R. The interatomic distances and bond angles are cited from X-ray data[9].

The respectrive frontier eletron density for r-th atom in