7. A. Mizuike, M. Hiraide, and T. Kanemtsu, *Japan Analyst*, **26**, 137 (1977).
8. W. J. Williams and A. H. Gillam, *Analyst*, **103**, 1239 (1978).
9. S. Nakashima and M. Yagi, *Anal. Chim. Acta*, **147**, 213 (1983).
10. N. Rothetein and H. Zeitlin, *Anal. Lett.*, **9**, 461 (1976).
11. A. Mizuike and M. Hiraide, *Bull. Chem. Soc. Jpn.*, **48**, 3753 (1975).
12. M. Hiraide and A. Mizuike, *Talanta*, **22**, 539 (1975).
13. M. Hiraide, A. Mizuike, and T. Suzuki, *Japan Analyst*, **18**, 519 (1977).
14. M. Aoyama, T. Hobo, and S. Suzuki, *ibid.*, **30**, 224 (1981).
15. M. Aoyama, T. Hobo, and S. Suzuki, *Anal. Chim. Acta.*, **129**, 237 (1981).
16. G, J. de Jong and U. A. Th. Brinkman, *ibid.*, **98**, 243 (1978):
17. K. B. Oldham, *Chem. Educ.*, **51**, 7 (1965).
18. X. Feng and D. E. Ryan, *Anal. Chim. Acta.*, **162**, 47 (1984).
19. M. Hiraide and A. Mizuike, *Rev. Chem.*, **VI(2)**, 151 (1982).
20. K. Matsusaki, *Anal. Chim. Acta.*, **141**, 233 (1982).
21. R. Kanipayer, *et al.*, *ibid.*, **166**, 39 (1984).
22. C. Veillon, K. Y. Patterson, and N. A. Bryden, *ibid.*, **164**, 67 (1984).

Reactive Intermediate in the Decomposition Reaction of Bis Diazo Compounds

Dae Dong Sung*, Yoo-Mee Park, Kyu Chul Kim, and Dong Kyu Park†

Department of Chemistry, Dong-A University, Pusan 604-714
†Department of Chemistry, Kyungsung University, Pusan 608-736

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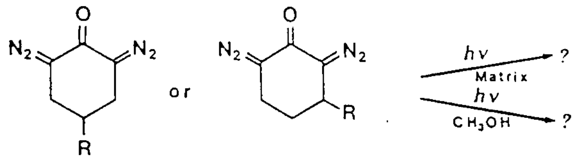
Photochemical extrusion reactions of dinitrogen from bis diazo compounds have been carried out by means of laser flash photolysis in argon matrix at low temperature. Photolytic reactions of bis diazo compounds in methanol have been also conducted by using a high-pressure mercury lamp at room temperature. Monocarbenes isolated in the matrix were identified by spectroscopic technique. The spectroscopic result for bis diazo cyclohexanone showed a triplet ketocarbene intermediate at the first step of the loss of nitrogen molecule from the substrate. The continuous decomposition reaction for bis diazo cyclohexanone in methanol at room temperature gave the Wolff rearrangement product.

Introduction

The spin state and molecular conformation of a novel hydrocarbon such as dicarbene are of considerable current interest in the area of synthetic organomagnetic materials.[1] Usually the organic molecules have closed-shell electronic structures, *i.e.* they are composed with singlet state of electrons having α-, and β-spins.[2] Most organic compounds are good electric insulators and are magnetically inactive,[3] that is, they have diamagnetic properties since they have the electrons of singlet state.

On the other hand there are some organic molecules that have open-shell eletronic structures that contains some spins unpaired.[4] Many of these molecules have one unpaired electron and exist as a doublet ground state. These species are called free radicals and are known to show paramagnetic properties.[5] The alignment of spins in molecular systems makes an issue when there is an interaction between two doublet centers, as in diradicals and radical pairs. The Coulombic repulsion between electrons lifts the zeroth-order degeneracy for these chemical species and gives to singlet and triplet states.[6] Wasserman *et al.*[7] reported that the dicarbene, consisting of two phenylcarbene units attached to the meta positions of a benzene ring, had a quintet ground state. This finding established unprecedented macroscopic spins of long-range order[8] in organic high-spin species and particularly in the possibility of organic ferromagnets.[9] The series of high-spin hydrocarbons have been detected by spectroscopic measurement for various aromatic poly-carbenes.[10] Despite their investigations, the study of decomposition of bis diazo compound is limited to a few spectroscopic observations.[11]

A bis diazo compound which is composed of non-Kékulé structure such as bis(diazo)cyclohexanone may be expected to show a different intermediate as triplet or quintet carbene from photolytic observation.



1 2

(R=*tert*-butyl, $-C_6H_5$, $-CH_3$)

In this paper the decomposition mechanism of bis diazo compound which has cyclohexanone ring system has been investigated by means of photolysis in argon matrix and methanol.

Experimental

General. Proton magnetic resonance (^1H-NMR) spectra were recorded on a Varian XL 400 spectrometer or a Varian XL 200 spectrometer in deuteriochloroform (unless otherwise noted) with tetramethylsilane as an interal standard.

Mass spectra (MS) were obtained from Hewlett-Packard 5996 GC/MS. Infrared absorption (IR) spectra were recorded on a Perkin-Elmer Model 683 grating spectrophotometer. Steady-state ultraviolet-visible (UV/vis) absorption spectra were recorded with UVIKON 940 spectrophotometer. Electron paramagnetic resonance (EPR) spectra were recorded on a Varian Associates E-4 (X-Band) spectrometer. Melting points were determined in the sealed capillary tubes employing a Büchi Schmelzpunkt-bestimmungsapparat. Analytical gas chromatograph (GS) was performed with a Shimadzu GC-RIA gas chromatography equipped with linear-temperature programmer and a flame ionization detector; 1.5-m silanized glass columns containing OV-17 (5%) or SE-30 on dichorodimethylsilane-treated Chromosorb W and with helium as the carrier gas at 20 psi.

Photolytic reaction was carried on by using a Hanovia 450 W high-pressure mercury lamp at room temperature in methanol. The laser flash photolysis apparatus used was the Laser photonics, LN 1000 Nitrogen Laser System which produces a pulsewidth of 600 ps duration with peak power output in excess of 2 MW and it average intensity limit was $\sim$20 mJ/cm^2·sec up to 50 mJ/cm^2·sec at 355 nm. The rise time of the system was measured as $\cong$5 ns, although this resolution could be achieved in practice using the laser.

The emission spectra were measured as a change in optical density. In a single-pulse irradiation, their optical densities represent the difference between the transient and its stable precursor, *e.g.*, the diazo compound.

In order to measure the lifetime of carbene we have used a sufficiently short pulse at 600 ps to allow direct lifetime measurements based on the fluorescence decay using a Instapec TM-XT detector Model 77160 and Stanford Research Systems Model SR 400 Gated Photon Counting System.

For all of the flash photolyic investigations, the samples of 2,6-bis(diazo)-cyclohexanones were contained in 10×10 mm (3 mL) graded seal quartz cuvettes. All samples were deaerated by purging with oxygen-free nitrogen.

Materials. 4-*tert*-butylcychohexanone, 3-methylcyclohexanone, 4-methylcyclohexanone, 4-phenylcyclohexanone, 3-phenylcyclohexanone, isoamylnitrite and sodium chloride were purchased from Aldrich Company and used without furthere purification.

Methanol was further purified by the literature method[12] for appropriate spectroscopic research.

4-*tert*-butyl-2,6-Bis(dizao)cyclohexanone. 4-*tert*-Butylcyclohexanone (3.856 g, 25 mmol) dissolved in 25 mL of dry diethyl ether was introduced to a 100 mL three-necked round-bottomed flask equipped with a magnetic stirring bar, a thermometer, a dropping funnel containing 1 mL of 37% hydrochloric acid and a reflux condenser fitted with a argon balloon. While the reaction mixture being stirred, the hydrochloric acid was added slowly during a period of *ca.* 30 min. the reaction was mildly exothermic, and the temperature was maintained at 5-10℃ in the ice bath by controlling the rate of addition the hydrochloric acid. After addition of the hydrochloric acid was completed, 7.32 mL of isoamylnitrite was added slowly during a period of *ca.* 20 min, while maintaining the temperature at 5-10℃.

The reaction mixture was stirred for a total of 1.5 hr after the additon was completed. And 1 mL of fresh pyridine was added to the reaction mixture. The crystalline was separated from the reaction mixtures by suction filtration and washed with water several times. The product was 4-*tert*-butyl-2,6 (oximino)cyclohexanone: Recrystallization from petroleum ether produced pale brown solid: IR (KBr disk) 3400-3200, 1720-1700, 1600, 1580 cm^{-1}, mp. 295℃.

4-*tert*-Butyl-2,6-bis(oximino)cyclohexanone (1.802 g, 8.62 mmol) was placed 500 mL three-necked flask equipped with magnetic stirrer, gas inlet, 50 mL of additional funnel and condenser. Dry nitrogen was slowly through the flask, and 68 mL of 15 N-NH_4OH and 25 mL of 5 N-NaOH were added during *ca.* 30 min. During this time the reaction mixture was maintained at 10-20℃ in the ice bath. After the addition was completed, then 25 mL of 5% sodium chlorite was added during *ca.* 10 min. Stirring was continued for 1 hr. The aqueous layer was separated from the ether and then extracted twice with ether. The ether solution was dried over anhydrous Na_2SO_4 for 10 hours, and then the solvent was removed on a vacuum drier. The product was reddish yellow solid: mp. 102-105℃; IR (KBr), 3190, 2815, 2100-2050, 1610, 1580, 1450, 1280 cm^{-1}, ^1H-NMR ($CDCl_3$) δ 0.98 (s, 9H), 2.4-2.7 (m, 4H).

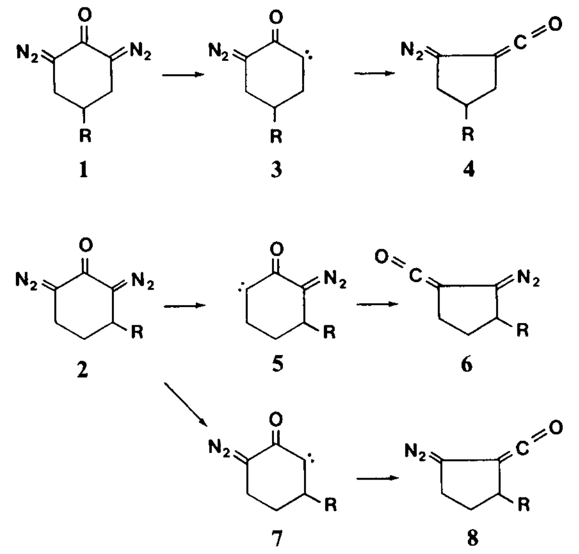
3-Methyl-2,6-Bis(diazo)cyclohexanone. The diazo compound was similarly prepared by substituting 3-methylcyclohexanone for 4-*tert*-butylcyclohexanone. This product (71% after recrystallization from ether/petroleum ether) was red solid. mp. 50-53℃; IR (KBr) 2980, 2705, 2100-2050, 1580, 1450, 1280 cm^{-1}, ^1H-NMR ($CDCl_3$) δ 1.19 (d, 3H-CH_3), 1.30-1.76 (m, 1H), 1.8-2.1 (m, 1H), 2.64 (d, 2H), 2.8-3.1 (m, 1H).

4-Methyl-2,6-Bis(diazo)cyclohexanone. The diazo compound was similarly prepared as the method 3-methyl-2,6-bis(diazo)cyclohexanone using 4-methylcyclohexanone. The product (76% after recrystallization using ether/petroleum ether) had yellowish red solid and mp. 62-64℃; IR (KBr) 3020, 2990, 2705, 2100-2050, 1610, 1570, 1450, 1285 cm^{-1}, ^1H-NMR ($CDCl_3$) δ 1.02 (s, 3H), 2.5-2.7 (m, 4H).

4-Phenyl-2,6-Bis(diazo)cyclohexanone. The diazo compound was similarly prepared by substituting 4-phenylcyclohexanone for 4-*tert*-butylcyclohexanone. The product (59% after separation from a liquid chromatograph) had a yellow liquid: IR (NaCl) 2980, 2770, 2100-2050, 1605, 1580, 1370, 1240 cm^{-1}, ^1H-NMR ($CDCl_3$) δ 2.6-2.8 (m, 4H), 7.4 (s, 5H).

3-Phenyl-2,6-Bis(diazo)cyclohexanone. The diazo compound was similarly prepared as the metod 3-phenyl-2,6-bis (diazo)cyclohexanone from 3-phenylcyclohexanone. The product (68% after separation from a liquid chromatograph) had a red-orange viscous oil; IR (NaCl) 3010, 2995, 2785, 2100-2050, 1710, 1620, 1580, 1410 cm^{-1}, ^1H-NMR ($CDCl_3$) δ 1.25-1.28 (m, 2H), 2.42-2.47 (m, 2H), 7.5 (s, 5H).

Low-temperature photolysis. Low-temperature spectra at 10 K were obtained by using a three-window (quartz) optical Dewar filled with liquid helium. the apparatus consists of three components: a refrigeration unit, a vacuum system, and a gas-handling system, and mounted on a movable cart. An Air Products Medel 202 Displex cryogenic refrigeration system, equipped with standard instrumentation



Scheme 1.

skirt and optical spectroscopy shroud Model DMX-IA. All apparatus and experimental technique used in this study of matrix-isolated reactive species have been applied by the method of Hess[13] and Kreil[14]. The sample was dissolved in dry methanol, placed in a long-necked Pyrex cuvett (*ca.* 3 mL), closed with a septum, and cooled in the liquid helium. After a baseline had been recorded, the sample was irradiated for several minutes in the spectrophotometer with a 450 W high-pressure mercury lamp or the laser beam. During the helium boil off the temperature was controlled by varying the current supplied to a resistance heater in the dewar. The temperature was monitored with a theromocouple and was maintained constant to within 1 degree.

Low-temperature EPR spectrum. The bis(dizao)cyclohexanone of *ca.* 0.5 mg in argon matrix of *ca.* 0.5 mL was placed in a quartz tube, helium was bubbled through the solution, and then it was capped with a septum and teflon tape. The sample was cooled to 10 K in a Dewar vessel which was equipped with quartz outer windows and sapphire inner windows and a liquid-helium transfer line, and then irradiated with a Hanovia 450 W high-pressure mercury lamp and the laser beam in the EPR cavity.

Results and Discussion

Spectroscopic behavior of excited ketocarbene. Irradiation ($\lambda>274$ nm) of 4-substituted-2,6-bis(diazo)cyclohexanone (**1**) was performed in argon at 10 K and gave first a diazoketene as shown in Scheme 1.

While irradiation of **2** isolated in argon at same temperature gave two isomers of monodiazoketene (**6**, **8**). Irradiations by various wavelengths (>416 nm, 415 nm, 364 nm, $\lambda>274$ nm) were tried to obtain the spectra.

Irradiation by shorter wavelengths of $\lambda>274$ nm showed only faster conversion of starting material. The diazoketenes (**4**, **6**, **8**) were easily identified by the intense band of infrared ketene stretching vibration ($\nu_{C=C=O}$) at 2118 and 2120 cm^{-1}. Irradiations ($\lambda>274$ nm, 8 min) of **1** gave a very strong triplet carbene spectra as observed at 10 K by ESR spectroscopy as shown in Figure 1.

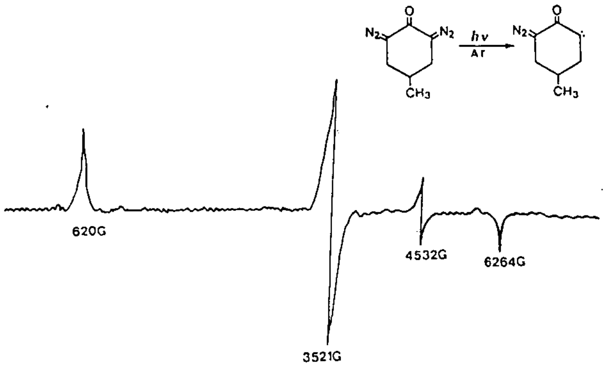
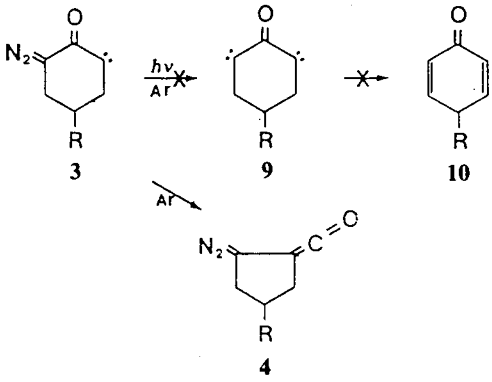


Figure 1. Electron spin resonance spectrum of 4-methyl-2-diazo cyclohexanone carbene (**3**) at 10 K.



Scheme 2.

Observation of the ESR signal of **5** and **7** also implies that the triplet state is either a minimum energy ground state or a state approaching to zero cal/mol of ground state in argon matrices at 10 K.

Furthermore irradiation by laser beam exhaustively to their triplet absorption species of **3**, **5** and **7**, the different spectra were not observed such as a quintet spectra at the X band ESR. If the quintet spectra were obtained in case of further irradiation of **3**, **5** and **7**, the quintet ESR spectra would be shown at the ground state of the dicarbene or at most a few small calories above the ground state. That is, in that case, there is a possibility to yield methyl-1,4-benzoquinone (**10**) from the quintet species. But ESR spectra are shown only triplet state. Therefore the possibility to produce the product (**10**) is excluded as shown in Scheme 2.

For the triplet carbene as shown in Figure 1 the zero-field splitting parameter (D/hc) and E/hc term based on the spin Hamiltonian[15] were determined by the magnetic interaction between the unpaired electrons as for **1**; (R=*tert*-butyl), D/hc=0.0821 cm^{-1}, E/hc=0.0243 cm^{-1}, for **1**; (R=Me), D/hc=0.0823 cm^{-1}, E/hc=0.0241 cm^{-1}, for **2**; (R=Me), D/hc=0.0842 cm^{-1}, E/hc=0.0231 cm^{-1} respectively. The D/hc values for mono carbenes of 2,6-cyclohexanone system are extremely lower than those comparing with other ground state triplet species,[7] while the values are close to dehydrobenzoquinodimethane (DBQM) like to diradical.[16] This observation is supporting the fact that there is no possible Kékulé structure of the quintet dicarbene containing a six membered ring which has a lower multiplicity.[15]

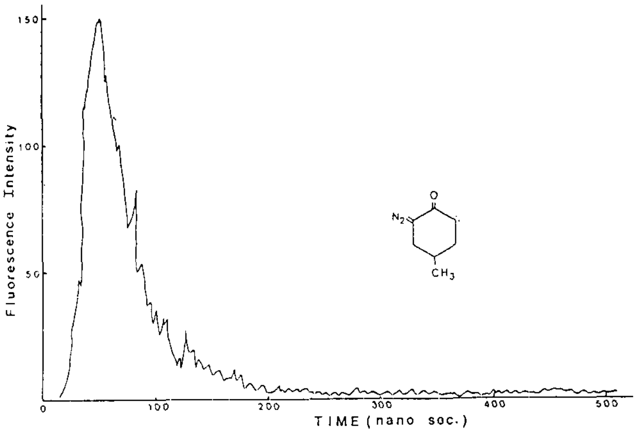
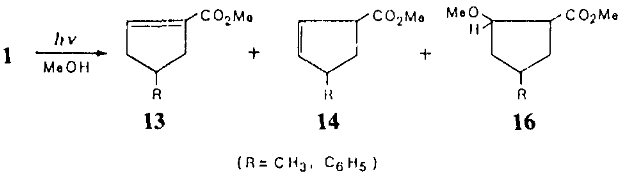


Figure 2. Fluorescence spectrum of excited 4-methyl-2-diazo cyclohexanone carbene (3) produced by excitation of the mono carbene in cyclohexane by 365 nm pulse at 10 K.



Scheme 3.

To find further evidence for the triplet character of mono carbenes (3, 5, 7) laser flash photolysis (LEP) was carried out at 10 K. A fluorescence spectrum obtained from the LFP is shown is Figure 2. The plot of the fluorescent intensity at 365 ± 5 nm as a function of nano second time scale is shown in Figure 2. The excited mono carbene (3) shows triplet-triplet fluorescence emission spectra at 10 K. A similar fluorescence spectra were obtained for **1** (R=*tert* butyl and phenyl) and for **2** (R=methyl and phenyl) as shown in Figure 2 at 45-50 ns. The fluorescence emission spectra were shown to be conformable with the triplet carbene state for **3**, **5**, and **7**.

The spectroscopic behavior for 3-substituted-2,6-bis(diazo) cyclohexanone (**2**) by using ESR and LFP methods showed a very similar trend of 4-substituted-2,6-bis(diazo)cyclohexanone (**1**) as triplet ketocarbene intermediate at the first step of the loss of nitrogen molecule from the substrate.

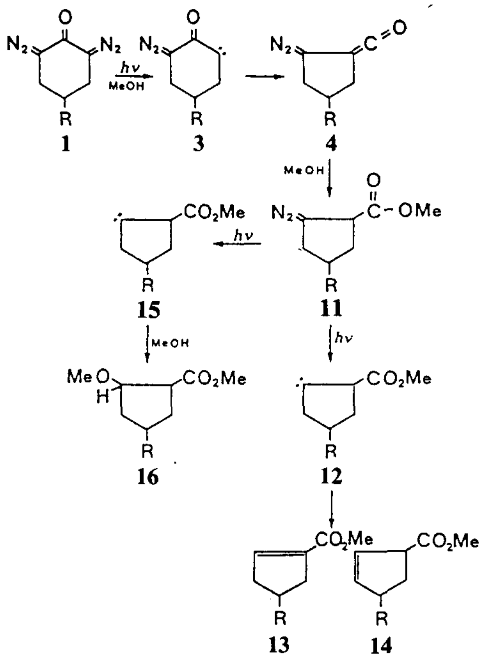
Continuous Decomposition Mechanism for Bis (diazo)cyclohexanone in Methanol. 4-Substitute-2,6-bis (diazo)cyclohexanones (**1**) have photolysed in methanol using a 450 W high-pressure mercury lamp at room temperature.

3-Methyl-1-methyl cyclopentenecarboxylate (**13**), 2-methyl-4-methyl cyclopentenecarboxylate (**14**) and 3-methyl-5-methoxy-1-methyl cyclopentanecarboxylate (**16**) were obtained as shown Scheme 3 as Wolff rearrangement product.

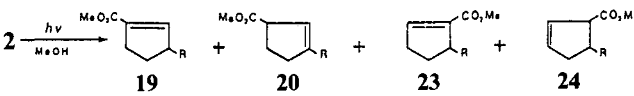
And 3-phenyl substituted **13**, **14**, and **16** products were obtained by the same photolytic method in methanol as shown in Scheme 3.

The reaction mechanism of the photolyses for **1** in pure methanol could be explained to prove an existence of the triplet carbenes at least in two steps through the photolytic reaction as shown Scheme 4.

Product analyses showed that the product **13** was a good yield comparing with **14** and **16**.



Scheme 4.



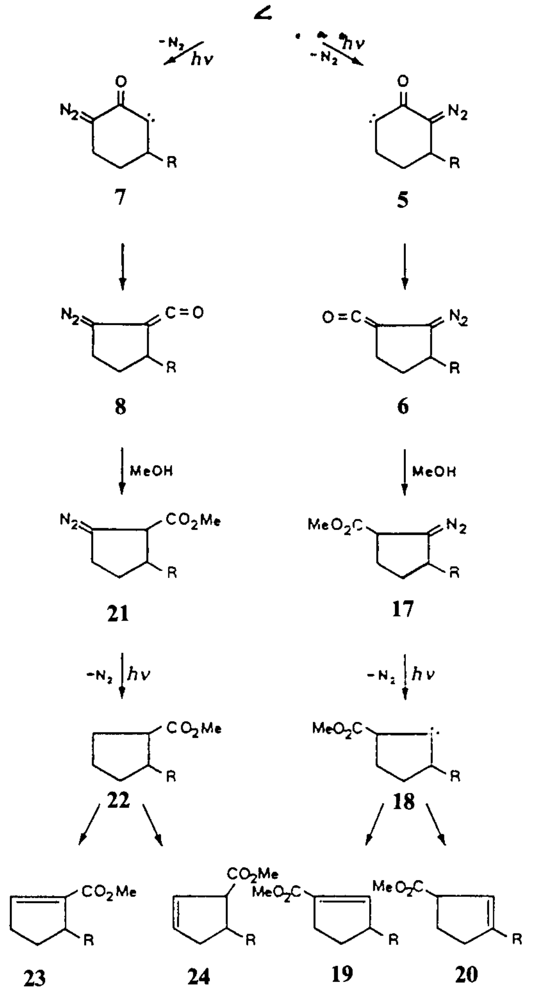
Scheme 5.

Another product analysis carried on the direct and triplet-sensitized photolysis of α-diazocarbonyl compounds by Tomioka[17] to postulate a concerted component occurring from the S-Z conformation and a nonconcerted component occurring from the S-E conformation. The experimental result of Tomioka reveals that the formation of Wolff rearrangement products was caused by triplet-sensitized irradiation.

In our experiments the Wolff rearrangement was observed nevertheless, there was no triplet sensitized conditions which diazo ketone took part in the step of ring contraction. The previous observation of ESR and LFP in this work illustrate that the participation of diazo ketone is excluded between the first step of simple nitrogen loss to give a ketocarbene and the second step of ring contraction to give ketene as shown as **3**, **4** in Scheme 4.

3-Substituted-2,6-bis(diazo)cyclohexanones (**2**) were also photolysed in methanol using a 450 W high-pressure mercury lamp at room temperature. 1-Carbomethoxy-3-methylcyclopentene (**19**), 3-carbomethoxy-1-methylcyclopentene (**20**), 2-carbomethoxy-3-methylcyclopentene (**23**) and 3-carbomethoxy-4-methylcyclopentene (**24**) were obtained from Wolff rearrangement as shown in Scheme 5. 3-Phenyl substituted **19**, **20**, **23**, and **24** products were also obtained by the same photolytic method in methanol as shown in Scheme 5.

The reaction mechanism of the photolyses for **2** in pure methanol could be also explained to prove an existence of the triplet carbenes in each steps when released the two molecules of nitrogen. Product analyses of the reaction shown in Scheme 5 revealed that the yield of compound



Scheme 6.

19 and **23** were greater than those of **20** and **24**. This trend is similar to the photolysis of **1**. The mechanism and spectroscopic results show that Wolff rearrangement proceeds through the steps of **5**→**6** and **7**→**8** in Scheme 6.

Our results are explainable that the ketocarbene (T_o) of triplet ground-state is produced as the primary photoproduct by photolysis of bis diazo ketone precursor as shown in Figure 3. The moment the ketocarbene (T_o) produced at lower energy state, T_o might be excited to the higher energy state of the ketocarbene (T_1). The ketocarbene T_1 exists as a higher vibronic state, which rapidly deactivates to different lower vibrational level by intersystem crossing conversion. In that case the intersystem crossing would be carried out nonradiative transition between two vibronic states of different multiplicity[18].

Presumably the singlet states exist three kind of energy states as S_I, S_{II} and S_{III} on the assumption that two spins occupy in the energy order as shown in Figure 3. The lower two singlet states of ketocarbenes, $S_I(n, \pi^*)$ and $S_{II}(\pi, \pi^*)$ would not convert to T_o state of ketocarbene in direct irradiation.[19] Because the necessary extrusion energy of the second intersystem crossing can be even more than the energy of the vertical singlet-triplet transition of the carbene.[19] In direct irradiation generally those carbenes which involve an excited state of S_I is ruled a spin-forbidden transition to convert T_o.[20]

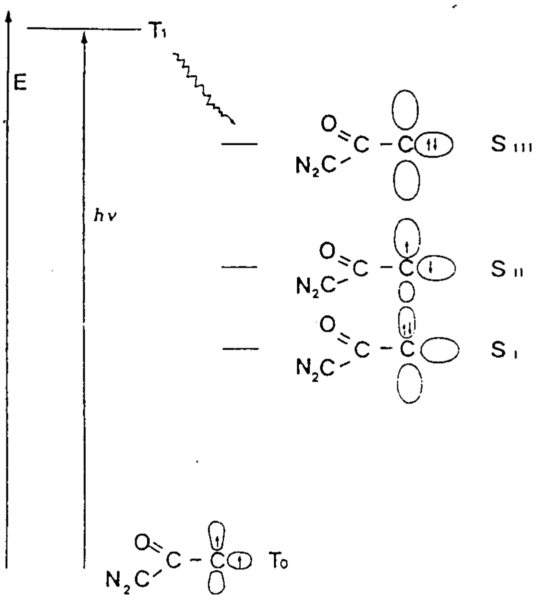


Figure 3.

Our result is satisfied that the conversions of T_o state→T_1 state→S_{III} state occur as shown in Figure 3 since the photochemical reaction was carried on by direct irradiation. However, a different result[20b] has been reported that the precursors of keto diazo compound is converted from S_I state to T_o state by the intersystem crossing. In that case the precursors of keto diazo compounds have very different energy and struture compared with our keto diazo compound. If the intersystem crossing of $S_I \rightarrow T_o$ easily occurs, the S_I state would exist a state of unreactive species and Wolff rearrangement would not be favorable to occur. Another evidence[21] has been reported that a concerted Wolff rearrangement proceeds *via* the lowest vibrational state of S_I diazoketone to T_o state in conformationally mobile systems. Those intermediates of carbene of S_I and T_o are different from our carbene since the intermediates of carbene are produced from mono diazo compound in comparison with what the carbenes in this experiment are produced from bis diazo compound. Therefore, it is reasonable that stereoelectronic factors in ketocarbenes (**3**, **5** and **7**) preclude ring contraction in the S_I state, thereby leading to trapping of the highly reactive, first-formed ketocarbenes. If a singlet state of S_I is favored to the intersystem crossing, the S_I state could not be oriented the first ring contraction[22] because the electronic state of S_I is the conformationally rigid ketocarbenes. Furthermore the singlet state of S_{II} is not appropriate because it does not possess[23] a vacant orbital as shown in Figure 3.

Therefore the Wolff rearrangement in photochemical extrusion reactions of bis diazo compounds (**1** and **2**) was proceeded through from α-diazo ketone to α-diazo ketene, and the step of ring contraction was facilitated by the higher energy singlet state of S_{III}.

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References

1. Y. V. Korshak, A. A. Ovchinnikov, A. M. Shapino, T. V. Medvedeva, and V. N. Spector, *JEPT Lett (Engl. Transl.)*, **43**, 399 (1986); I. Fujita, T. Yoshio, T. Takeji, T. Kinoshita, and K. Itoh, *J. Am. Chem. Soc.*, **112**, 4074 (1990); J. B. Torrance, S. Oostra, and A. Nazzal, *Synth. Met.*, **19**, 709 (1987); J. S. Miller, A. J. Epstein, and W. M. Reiff, *Chem. Rev.*, **88**, 207 (1988).
2. Y. Teki, T. Takui, K. Itoh, H. Iwamura, and K. Kobayashi, *J. Am. Chem. Soc.*, **108**, 2147 (1986).
3. H. Iwamura, *Adv. Phy. Org. Chem.*, **26**, 180 (1990).
4. W. T. Borden, "Diradicals", Wiley, New York Chap 1, (1982).
5. D. Bethell and M. R. Brinkman, *Adv. Phy. Org. Chem.*, **10**, 53 (1973).
6. A. R. Lepley and G. L. Closs, "*Chemically Induced Magnetic Polarization*" Willy, New York (1973).
7. E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinsky, *J. Am. Chem. Soc.*, **89**, 5076 (1967).
8. J. Brickman and G. Kothe, *J. Chem. Phys.*, **59**, 2807 (1973); T. Takui and K. Itoh, *Chem. Phys. Lett.*, **50**, 1251 (1978).
9. N. Mataga, *Theor. Chim. Acta.*, **10**, 372 (1968); A. A. Ovchinnikov, *Theor. Chim. Acta.*, **47**, 297 (1978); M. Schwoerer, R. A. Huber, and W. Hartl, *Chem. Phys. Lett.*, **55**, 97 (1981).
10. T. Takui and K. Itoh, *Chem. Phys. Lett.*, **19**, 120 (1973); K. Itoh, *Pure. Appl. Chem.*, **50**, 1251 (1978); Y. Teki, T. Takui, H. Yagi, K. Itoh, and H. Iwamura, *J. Chem. Phys.*, **83**, 539 (1985); S. Murata, T. Sugawara, and H. Iwamura, *J. Am. Chem. Soc.*, **109**, 1266 (1987).
11. R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **88**, 3527 (1966); H. Meier and I. Menzer, *Synthesis*, 215 (1971).
12. E. C. Evers and A. G. Knox, *J. Am. Chem. Soc.*, **73**, 1739 (1951).
13. T. C. Hess, Ph. D. Dissertation, University of California, Los Angeles, CA (1978).
14. C. L. Kreil, Ph. D. Dissertation, University of California, Los Angeles, CA (1983).
15. K. Itoh, *Pure. Appl. Chem.*, **50**, 1251 (1978); H. Iwamura, *Pure. Appl. Chem.*, **59**, 1595 (1987).
16. K. Itoh, *Chem. Phys. Lett.*, **1**, 235 (1967).
17. H. Tomioka, H. Okuno, and Y. Izawa, *J. Org. Chem.*, **45**, 5278 (1980); H. Tomioka, M. Kondo, and Y. Izawa, **46**, 1090 (1981).
18. J. Kopecky, "*Organic Photochemistry*: A Visual Approach", VCH Publishers, Inc., 33 (1992).
19. For reviews of the photochemistry of diazo compound, see: (a) H. Dürr, In "*Methoden der Organicschen Chemie (Houben-Weyl)*." G. Thieme: Stuttgart, **Vol. 4/5b**, 1158 (1975); (b) H. Dürr, *Topics Curr. Chem.*, **55**, 87 (1976); (c) M. Regitz and G. Maas, "*Diazo compounds: Properties and Synthesis*", Academic, New York (1986); (c) Y. Z. Li and G. B. Schuster, *J. Org. Chem.*, **52**, 4460 (1987).
20. (a) H. Meier and K. P. Zeller, *Angew. Chem. Int. Ed. Engl.*, **14**, 32 (1975); (b) W. Ando, In "*The Chemistry of the Diazonium and Diazo Group*", S. Patai ed., Wiley, New York, Part 1, 458 (1978); (c) M. Regitz and G. Mass, "*Diazo compounds: Properties and Synthesis*", Academic Press, Orlando, Florida, 185 (1986).
21. C. Marfisi, P. Verlaque, D. Davidovics, J. Pourcin, L. Pizzala, J.-P. Acard, and H. Bodot, *J. Org. Chem.*, **48**, 533 (1983).
22. W. J. Bouma, R. H. Nobes, L. Radom, and C. E. Woodward, *J. Org. Chem.*, **47**, 1869 (1982).
23. S.-J. Chang, B. K. Ravi Shankar, and H. Shechter, *J. Org. Chem.*, **47**, 4226 (1982).

Observation of Electronic Emission Spectra of CH_3S

Sang Kuk Lee

Department of Chemistry, College of Natural Sciences, Pusan National University, Pusan 609-735

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The combination of Fourier Transform spectroscopy with a technique of supersonic expansion has been employed to examine the vibronic structure of the transition $A^2A_1 \rightarrow X^2E$ of CH_3S radical. CH_3S was produced by an electric *dc* discharge of the precursor $(CH_3)_2S$. The emission spectrum of CH_3S shows extensive progressions of CS stretching frequencies in the transitions. The molecular parameters describing the vibrational structure of CH_3S have been determined with high accuracy from the analysis of the emission spectrum.

Introduction

For a long time, alkylthio radicals (RS·) have been reported[1-3] to be an intermediate in combustion and atmospheric chemistry of organosulfur compounds. Theses compounds also play an important role in the atmospheric sulfur cycle and contribute to the acidic rain problem. Particularly, CH_3S is considered an important intermediate in oxidative reaction