with methylene chloride (3 × 50 mL), and the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuum to give a crude product which was further purified by column chromatography on silica gel to give tetraphenylethylene (0.32 g, 39% yield).

Preparation of ^{13}C-Labeled Diphenyldiazomethane. ^{13}C-Labeled benzoic acid (Aldrich) was reacted with phosphorus pentachloride using a literature procedure.[14] The resulting benzoyl chloride was refluxed in dried benzene in the presence of aluminum trichloride to give ^{13}C-labeled benzophenone. The corresponding benzophenone hydrazone and diphenyldiazomethane were then obtained using a literature procedure.[11]

Reaction of Trityl Cation with ^{13}C-Labeled Diphenyldiazomethane. A 5-mm NMR tube was charged with trityl tetrafluoroborate (20 mg), and deuteriated methylene chloride (1 mL) was added. The spectrum of the trityl cation was taken at −20 °C. ^{13}C-Labeled diphenyldiazomethane (30 mg) was then added into the NMR tube at −78 °C. The NMR tube was briefly shaken to complete the reaction, and the reaction mixture was immediately analyzed by ^{13}C NMR spectroscopy at −20 °C.

Reaction of Nitrosonium Tetrafluoroborate with Diphenyldiazomethane. To an ultrasound-agitated suspension of nitrosonium tetrafluoroborate (10 mmol) in dry 1,1,2-trifluorotrichloroethane (Freon-113) (10 mL) was added dropwise a solution of diphenyldiazomethane (5 mmol) in dry Freon-113 (10 mL) over a period of 15 min. After addition, the reaction mixture was sonicated further for an hour. Subsequently the reaction mixture was quenched with water. Extraction was carried out with dichloromethane (3 × 50 mL), and the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuum to leave a crude material which was purified via column chromatography on silica gel (hexane eluent) to afford tetraphenylethylene (0.58 g, 70% yield). Sonication was necessary for the reaction to occur.

Reaction of Iodine with Diphenyldiazomethane. A mixture of iodine (10 mmol) and benzophenone hydrazone (5 mmol) was suspended in 10 mL of dry 1,1,2-trifluorotrichloroethane (Freon-113) and agitated with ultrasound for 3 h. The reaction mixture was then quenched with water. After being extracted with dichloromethane (3 × 50 mL), the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuum to leave a crude product which was further purified via column chromatography on silica gel to give tetraphenylethylene (0.42 g, 51% yield).

Reaction of Nitrosonium Tetrafluoroborate with Diphenylketene. To an ultrasound-agitated suspension of nitrosonium tetrafluoroborate (5 mmol) in 10 mL of dry 1,1,2-trifluorotrichloroethane (Freon-113) was dropwise added a solution of diphenylketene (10 mmol) in dry Freon-113 (10 mL) over a period of 15 min. After completion of the addition of ketene, the reaction mixture was further sonicated for 1 h and was then quenched with water. After being extracted with dichloromethane (3 × 50 mL), the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuum to leave a crude product which was purified via column chromatography on silica gel to give tetraphenylethylene (0.22 g, 27% yield).

Reaction of Iodine with Diphenylketene. Iodine (5 mmol) and diphenylketene (5 mmol) were treated in Freon-113 solvent (10 mL) as above, and the reaction mixture after workup and purification gave tetraphenylethylene (0.15 g, 18% yield).

Protonation of Diphenyldiazomethane. To a 5-mm NMR tube charged with diphenyldiazomethane (20.0 mg, 0.1 mmol) and freshly distilled SO_2ClF (1.0 mL) was added fluorosulfonic acid/antimony pentafluoride (0.2 mL) at −60 °C (in a dry ice/acetone external cold bath). After vigorous stirring, a homogeneous solution was obtained. The ^{13}C NMR spectrum was obtained at −60 °C and gave absorptions at $\delta(^{13}C)$ 200.6, 142.2, 129.5, 128.7, and 127.5.

Protonation of Diphenylketene. To a 5-mm NMR tube charged with diphenylketene (20.0 mg, 0.1 mmol) and freshly distilled SO_2ClF (1.0 mL) was added fluorosulfonic acid/antimony pentafluoride (0.2 mL) and maintained at −60 °C (using a dry ice/acetone external cold bath). After vigorous shaking, a clear solution was obtained. ^{13}C NMR spectroscopy at −60 °C showed absorptions at $\delta(^{13}C)$ 154.7, 139.8, 129.5, 128.7, 127.8, and 48.9, which correspond to diphenylacetylium ion.

Protonation of Di-*tert*-butylketene. To a 5-mm NMR tube charged with di-*tert*-butylketene (20.0 mg; 0.1 mmol) and freshly distilled SO_2ClF (1.0 mL) was added fluorosulfonic acid/antimony pentafluoride (0.2 mL) at −60 °C. After vigorous shaking, a homogeneous solution was obtained. ^{13}C NMR at −60 °C showed absorptions at $\delta(^{13}C)$ 154.1, 49.8, 41.3, and 26.6, corresponding to the di-*tert*-butyl acetylium ion. Upon warming the solution, rearrangement occurred with a loss of CO to give a mixture of *tert*-butyl and *tert*-amyl cations (**22** and **23**).

Acknowledgment. Support of our work by the National Institute of Health is gratefully acknowledged.

Photochemistry of (2-Nitrophenyl)diazomethane Studied by the Matrix Isolation Technique. (Nitrophenyl)carbene to (Carboxylphenyl)nitrene Rearrangement by Successive Reduction of the Nitro Group with the Carbenic Center

Hideo Tomioka,* Naoki Ichikawa, and Kazunori Komatsu

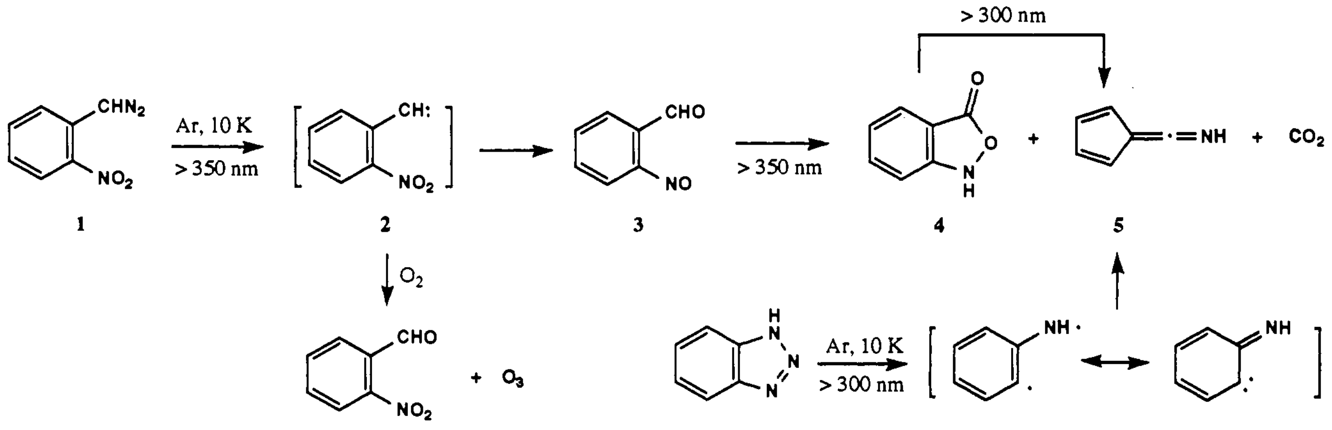
Contribution from the Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan. *Received April 7, 1992*

Abstract: Irradiation (λ > 350 nm) of (2-nitrophenyl)diazomethane (**1**) matrix-isolated in Ar at 10 K provided 2-nitrosobenzaldehyde (**3**) presumably as a result of intramolecular oxygen migration in (2-nitrophenyl)carbene (**2**). Upon further irradiation (λ < 350 nm), **3** was decomposed to give a mixture of 2,1-benzisoxazol-3(1*H*)-one (**4**) and carbonylcyclopentadiene imine (**5**) along with CO_2. The oxazolone (**4**) underwent decarboxylation to give **5** upon irradiation with shorter wavelength light (λ > 300 nm) but not at longer wavelength (λ > 350 nm), suggesting **4** is not the direct precursor for **5** in the photolysis of **3**. Irradiation (λ > 350 nm) of (4-*n*-butyl-2-nitrophenyl)diazomethane (**1b**) under similar conditions resulted in the formation of carbonyloximinocyclohexadienylidene (**7**) which then produced the oxazolone (**4b**) and the imine (**5b**) upon further irradiation, suggesting that a 1,4-biradical generated as a result of abstraction of H at the ortho position by the photoexcited nitroso group was involved in the reaction of **3** forming **4**. (2-Carboxyphenyl)nitrene (**9**) generated by 1,4-OH shift in the 1,4-biradical was postulated as an intermediate leading to **5**, and this was actually demonstrated by independent generation of **9** by the photolysis of 2-azidobenzoic acid (**8**).

Since the pioneering work by Chapman and his co-workers,[1] matrix isolation techniques have shown their greatest power for investigating carbene chemistry.[2] These techniques not only enable us to observe and characterize these highly reactive species

0002-7863/92/1514-8045$03.00/0

Scheme I



but also reveal fascinating aspects of their chemistry which has never been observed under ambient conditions.[3] For instance, phenylcarbene itself is trapped and therefore is observed directly by conventional spectroscopic means under these conditions.[4] Upon photoexcitation, it undergoes ring-expansion to produce 1,2,4,6-cycloheptatetraene.[4] On the other hand, phenylcarbenes bearing reactive groups near the carbenic center usually afford new reactive intermediates as a result of intramolecular interaction between the carbenic center and the proximate reactive groups. Thus, 2-tolylmethylene undergoes photorearrangement to produce 4-methylcycloheptatetraene and 2-xylylene[5] which can be considered as an intermediate involved in thermal rearrangement of isomeric tolylmethylenes. (2-(Methoxycarbonyl)phenyl)carbene, on the other hand, is trapped by the carbonyl group to yield the carbonyl ylide,[6] which has been assumed[7] as a key intermediate in the reaction of the carbene in fluid solution.

As an extension of our works[6,8] on the intramolecular interaction of carbenic center with proximate functional groups thereby generating a new reactive species, we investigated the behavior of (*o*-nitrophenyl)carbene (**2**) in an Ar matrix at 10 K and found that the carbene center underwent interesting oxygen "uptake" reactions from the proximate nitro group, ultimately reducing the nitro group up to nitrene. An important role of a vibrationally excited state of the reactive intermediates was also found.

Results

Irradiation ($\lambda > 350$ nm) of (2-nitrophenyl)diazomethane (**1**) matrix-isolated in Ar at 10 K was monitored by infrared spectroscopy, which revealed a rapid and simultaneous disappearance of both absorption bands due to diazo (2072 cm^{-1}) and nitro (1614, 1570, 1528, and 1484 cm^{-1}) groups and growth of new strong bands at 1708, 1516, 1137, and 768 cm^{-1} along with other minor bands (Figure 1). Simultaneous disappearance of both diazo and nitro absorption implies that carbene generated by photolysis of **1** is trapped by the nitro group at the ortho position, and appearance of new carbonyl absorption indicates the trapping reaction must be oxygen transfer from the nitro group to the carbenic center forming 2-nitrosobenzaldehyde (**3**). This was unambiguously confirmed by the direct comparison of the photoproduct spectrum with that of authentic matrix-isolated sample prepared[9] independently.

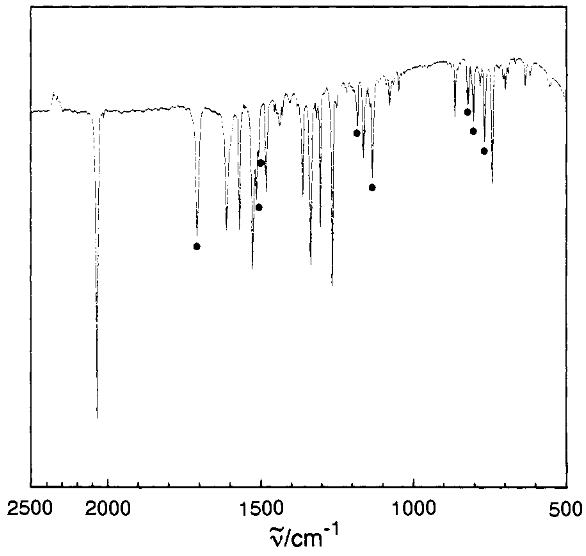


Figure 1. IR spectrum of (2-nitrophenyl)diazomethane (**1**) in Ar at 10 K after 10-min irradiation at $\lambda > 350$ nm. Bands marked with full circles are assigned to 2-nitrosobenzaldehyde (**3**), and other peaks are due to **1**.

These results demonstrate that (2-nitrophenyl)carbene (**2**) generated in matrix undergoes oxygen transfer from the nitro group at the ortho position to the carbenic center. We were not able to detect the absorption bands ascribable to **2** during irradiation causing the transformation of **1** to **3**. However, its intervention was shown by trapping experiments using O_2. Thus, irradiation of **1** in Ar doped with 20% O_2 resulted in the formation of 2-nitrobenzaldehyde along with O_3 at the expense of **3**. It is well-known[10,11] that carbenes with triplet ground state generated in an oxygen-doped matrix generally react with the doped O_2 to give the corresponding carbonyl oxides which, at very high O_2 concentration (>5%), reacts with O_2 to form the ketones and O_3. All attempts to observe **2** by careful irradiation of **1** with a visible

---

(1) Chapman, O. L. *Pure Appl. Chem.* **1979**, *51*, 331.

(2) (a) Sheridan, R. S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker Inc.: New York, 1987; Vol. 8, pp 159–248. (b) Dunkin, I. R. *Chem. Soc. Rev.* **1980**, 9, 1.

(3) (a) *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1973, 1975; Vol. 1 and 2. (b) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971. (c) *Methoden der Organischen Chemie*; Regitz, M., Ed.; (Houben-Weyl); Thieme: Stuttgart: 1989; Vol. E 19b.

(4) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779.

(5) Chapman, O. L.; Johnson, J. W.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1988**, *110*, 501.

(6) (a) Murata, S.; Ohtawa, Y.; Tomioka, H. *Chem. Lett.* **1989**, 853. (b) Tomioka, H.; Ohtawa, Y.; Murata, S. *Nippon Kagaku Kaishi* **1989**, 1431.

(7) For instance: Ibata, T.; Motoyama, T.; Hamaguchi, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2298.

(8) (a) Tomioka, H.; Hirai, K.; Tabayashi, K.; Murata, S.; Izawa, Y.; Inagaki, S.; Okajima, T. *J. Am. Chem. Soc.* **1990**, *112*, 7692. (b) Tomioka, H.; Nunome, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 1243. (c) Tomioka, H.; Hirai, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1611. (d) Tomioka, H.; Kobayashi, N.; Murata, S.; Ohtawa, Y. *J. Am. Chem. Soc.* **1991**, *113*, 8771.

(9) Bakke, J. M.; Engan, H. J. *Acta Chem. Scand.* **1978**, *B32*, 230. Bakke, J. M. *Acta Chem. Scand.* **1974**, *B28*, 645.

(10) See, for review: Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344.

(11) (a) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1213. (b) Dunkin, I. R.; Shields, C. J. *J. Chem. Soc., Chem. Commun.* **1986**, 154. (c) Bell, G. A.; Dunkin, I. R.; Shields, C. J. *Spectrochim. Acta* **1985**, *41A*, 1221. (d) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Faraday Trans.* **1985**, *81*, 725. (e) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 255. (f) Sander, W. *Spectrochim. Acta* **1987**, *43A*, 637. (d) Sander, W. *J. Org. Chem.* **1988**, *53*, 125, 2091. (e) Sander, W. *J. Org. Chem.* **1989**, *54*, 333. (i) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517. (j) Murata, S.; Tomioka, H.; Kawase, T.; Oda, M. *J. Org. Chem.* **1990**, *55*, 4502.

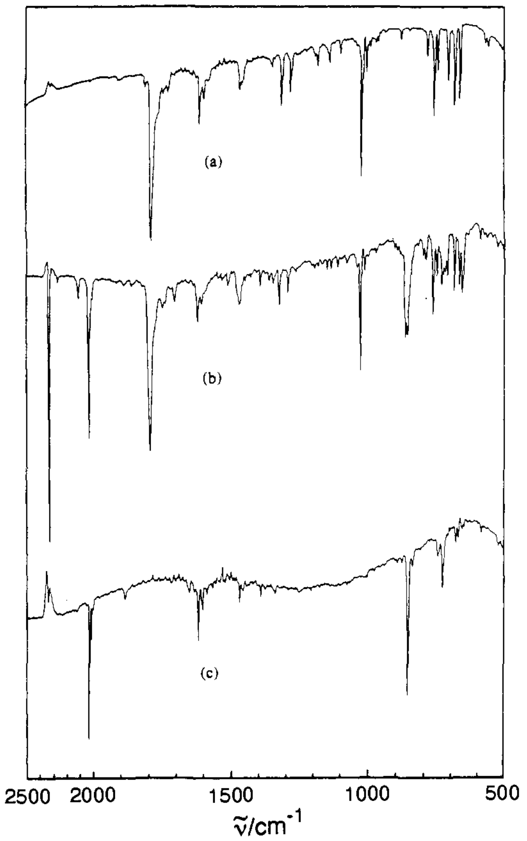


Figure 2. (a) IR spectrum of 2,1-benzisoxazol-3(1*H*)-one (**4**) matrix-isolated in Ar at 10 K. (b) IR spectrum obtained by irradiation ($\lambda >$ 350 nm) of **3** in Ar at 10 K. (c) IR spectrum of carbonylcyclopentadiene (**5**) obtained by irradiation ($\lambda >$ 245 nm) of 1,2,3-benzotriazole in Ar matrix at 10 K.

light or flash irradiation,[12] however, were unsuccessful, suggesting that the oxygen transfer reaction is very fast. The results agree with the experimental observations and theoretical calculation that α-nitrocarbene is very labile and rearranges to nitrosoformaldehyde with nearly zero activation energy.[13,14]

The nitrosobenzaldehyde (**3**) was photolabile under these conditions and decomposed upon continued irradiation ($\lambda >$ 350 nm) to produce two *major* products simultaneously, one exhibiting a strong band at 1800 cm^{-1} due to carbonyl group, with the other at 2040 cm^{-1} probably owing to cumulenic double bond, along with CO_2 (2342 cm^{-1}) (Figure 2). Several attempts to compare the product spectra with those of the authentic compounds of possible reaction products soon revealed that the former products was 2,1-benzisoxazol-3(1*H*)-one (**4**),[15] while the latter was carbonylcyclopentadiene imine (**5**),[16] which was generated in situ by the photolysis of 1,2,3-benzotriazole in Ar matrix at 10 K (Figure 2). These products were photostable under these conditions; extended irradiation ($\lambda >$ 350 nm) of the photomixtures did not result in any appreciable changes in the spectra (Scheme I).

Discussion

Thus, overall photoreactions of **1** appear to be quite simple in terms of product analysis since all of the photoproducts were unambiguously assigned by the direct comparison of their spectrum with those of the authentic compounds. However, the mechanism of the reaction turned out to be somewhat complicated. First, the formation of **4** from **3** resulting in a net insertion of N=O bond into the C–H bond of aldehyde must include some intermediates since it is not easy to draw a simple direct pathway for this transformation. The observations that weak absorptions which did not coincide with those of **4** and **5** grew and disappeared during the transformation suggest that other minor products were also formed and/or that intermediates involved in the transformation appeared. Second, what is the intermediate forming **5** from **3** under these conditions? By analogy with the photolysis[16] of benzotriazole, **5** could be formed by photodecarboxylation of **4** by way of iminocyclohexadienylidene intermediate.[17] The idea was supported by the observation that the formation of **5** was accompanied by that of CO_2, the ratio being roughly constant during the photolysis. Control experiments showed that irradiation of **4** in Ar matrix at 10 K with the shorter wavelength light (λ > 300 nm) actually produced **5** with CO_2, while similar irradiation with the longer wavelength light ($\lambda >$ 350 nm), where **3** produced **5** and CO_2, resulted in no appreciable decomposition of **4**, suggesting that **4** was not a precursor for **5** at least in the photochemical transformation of **3** with the $\lambda >$350 nm light. The following control experiments were carried out to find clues to these mechanistic problems.

It has been warned[18] that photochemical processes in noble gas matrices sometimes result in the generation of reactive intermediates in vibrationally excited states which undergo subsequent reactions faster than they cool off to the thermally relaxed states and therefore an intermediate supposed to be involved often becomes elusive even under these conditions. One of the effective ways to decrease the rate of reaction in a vibrationally hot species is to introduce an alkyl chain in the reactive species thereby increasing the number of vibrational modes. Thus, in order to obtain information along this line we investigated the photochemistry of (4-*n*-butyl-2-nitrophenyl)diazomethane (**1b**) in Ar matrix, which actually provided an important clue to the mechanism.

Attempts to Cool Vibrationally Excited States. Detection of Oxime Ketene (7). Irradiation ($\lambda >$ 350 nm) of **1b** matrix-isolated in Ar at 10 K again afforded the corresponding nitrosobenzaldehyde (**3b**) as the major product. Absorptions ascribable to the carbene were not apparent again. Continued irradiation (λ > 350 nm) of **3b** afforded a product showing strong, sharp absorption at 2094 cm^{-1}, which increased with the 3630 cm^{-1} band, reached a maximum within 1 h irradiation, and then gradually decreased with concurrent appearance of peaks due to isoxazolone (**4b**) and imine (**5b**), along with strong sharp absorption appearing at 2114 cm^{-1}. The last sharp band increased monotonically and did not appreciably lead to **4b** or **5b** at least in time ranges where the initially formed sharp band (2094 cm^{-1}) underwent decomposition (Figure 3).

The initial photoproduct from **3b** exhibiting bands at 2094 and 3630 cm^{-1}, presumably due to ketene and hydroxy groups, respectively, was assigned as oxime ketene derivative (**7b**), whose formation can be reasonably interpreted in terms of the intramolecular hydrogen abstraction by the excited nitroso group, followed by an electron redistribution, by analogy with the similar photochemical transformation of 2-nitrobenzaldehyde leading to *o*-nitrosobenzoic acid.[19,20] This assignment was then unambiguously supported by the generation of **7** from an independent source (vide infra). The subsequent spectral changes upon irradiation can be reasonably explained as indicating that **7** either

---

(12) Chapman reported[5] that, in the photolysis of *o*-tolyldiazomethane in argon matrix, long wavelength irradiation (>470 nm) or flash irradiation (>200 nm, 1.0 min) produced high conversion of triplet *o*-tolymethylene which otherwise rearranged to *o*-xylylene and 1-methylcycloheptatetraene very efficiently.

(13) (a) O'Bannon, P. E.; Carroll, P. J.; Dailey, W. P. *Tetrahedron Lett.* **1988**, *29*, 6031. (b) O'Bannon, P. E.; Dailey, W. P. *Tetrahedron Lett.* **1988**, *29*, 987. (c) O'Bannon, P. E.; Dailey, W. P. *Tetrahedron Lett.* **1989**, *30*, 4197. (d) O'Bannon, P. E.; Dailey, W. P. *J. Org. Chem.* **1989**, *54*, 3096.

(14) Franck-Neumann, M.; Miesch, M. *Tetrahedron Lett.* **1984**, *25*, 2909.

(15) Cohen, T.; Gray, W. F. *J. Org. Chem.* **1972**, *37*, 741.

(16) Tsujimoto, K.; Ohashi, M.; Yonezawa. T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 515.

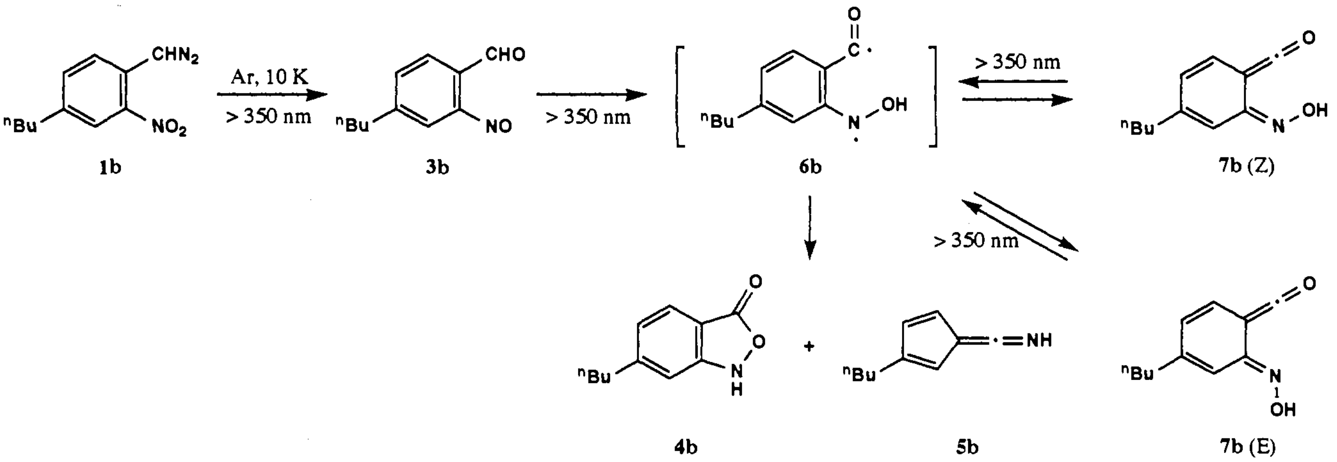
(17) Photofragmentation of phthalide in low-temperature matrices, however, predominantly resulted in loss of CO to give benzaldehyde. Dunkin, I. R.; MacDonald, J. G.; Martin, G. S. *Tetrahedron Lett.* **1983**, *24*, 4373.

(18) LeBlanc, B. F.; Sheridan, R. S. *J. Am. Chem. Soc.* **1988**, *110*, 7250.

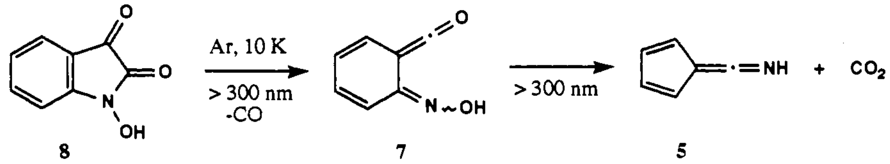
(19) Ciamician, G.; Silber, P. *Chem. Ber.* **1901**, *34*, 2640.

(20) (a) de Mayo, P. *Adv. Org. Chem.* **1960**, *2*, 367. (b) de Mayo, P.; Reid, S. T. *Quat. Rev. Chem. Soc.* **1961**, *15*, 393. (c) Morrison, H. A. *The Chemistry of the Nitro and Nitroso Group*; Feuer, H., Ed.; Wiley; New York; 1970; Part I, p 185. (d) George, M. V.; Scaiano, J. C. *J. Phys. Chem.* **1980**, *84*, 492, and references cited therein.

Scheme II



Scheme III



undergoes ring closure[21] to form the oxazolone (**4**) or is isomerized to the geometrical isomer. Probably, the first formed insomer of **7** which can produce **4** must be the *Z* isomer since in this isomer oxime hydroxy and ketene groups are suitably situated for the cyclization, while the slowly formed 2114-cm^{-1} isomer accumulating during irradiation must be the *E* isomer. Plots of absorption intensities of each product as a function of irradiation time indicate, however, that **7**(*E*) decomposed very slowly, after it reached a maximum, to result in an increase in the absorptions due to **4** and **5**. This suggests that **7**(*E*), when exposed to light, is excited to give **4** and **5** either by way of **7**(*Z*) or in its excited states (Scheme II).

The observations clearly suggest that intermediates involved in the photochemical transformation of **3** to **4** and **5** must include **7**. Careful examination of the spectral changes during irradiation of **3** producing **4** and **5** reveals that weak but distinct absorptions appeared and disappeared in 2080–2100-cm^{-1} regions in the reaction. Unambiguous evidence for the identification and intervention of **7** in the reaction was obtained by generating this intermediate from an independent precursor. Thus, irradiation ($\lambda > 300$ nm) of *N*-hydroxyisatine (**8**) matrix-isolated in Ar at 10 K resulted in the appearance of new band at 2116 cm^{-1} which increased with increase in the absorption due to CO (2136 cm^{-1}). The formation of CO in the mixture strongly suggests that the isatine undergoes photodecarbonylation. The band at 2116 cm^{-1} is then attributable to the ketene of **7**. Continued irradiation resulted in a gradual decrease in the absorption of **7** and concurrent growth of a new ketene band at 2042 cm^{-1} presumably due to **5** along with CO_2 (2342 cm^{-1}) (Figure 4). Although we were not able to observe the formation of **4** in this photoreaction obviously due to its photolabile nature under >300-nm light irradiation, these observations not only confirmed the assignment for **7** but also demonstrated its intervention in the photochemical transformation of **3** to **4** and **5** (Scheme III).[21a]

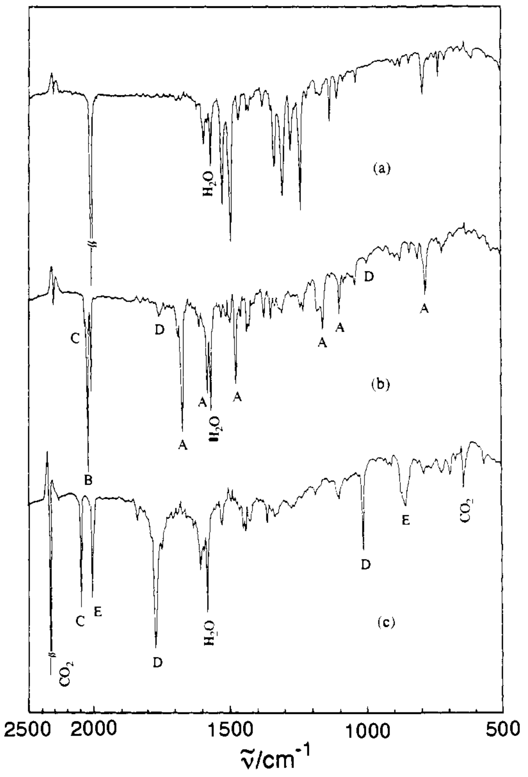


Figure 3. (a) IR spectrum of (4-butyl-2-nitrophenyl)diazomethane (**1b**) matrix-isolated in Ar at 10 K. (b) and (c) Spectrum obtained after irradiation of (a) for 25 min and 22.5 h at $\lambda > 350$ nm, respectively. Bands labeled A, D, and E are due to **3b**, **4b**, and **5b** respectively, and B and C are assigned to the oxime ketene **7b**(*Z*) and **7b**(*E*).

Appreciable formation of **7** by introducing an alkyl chain then suggests that a reactive intermediate involved in the photochemical transformation from **3** to **4** and **5** is subject to cooling off. What is the intermediate undergoing vibrational decay, then? The oxime ketene (**7**) itself seems to be an intermediate since its cyclization leading to **4** might proceed thermally. 1,4-Biradical (**6**) generated by the intramolecular H abstraction by the excited nitroso group would be a more probable intermediate undergoing vibrational decay. Thus, the nascent biradical should be generated with excess vibrational energy which makes this reactive species undergo the subsequent reaction forming **4** and **5** in competition with the electron redistribution decaying to **7**. Introduction of the vibrational channels in the biradical intermediate should decrease the

---

(21) (a) Gebicki, J.; Kuberski, S. *J. Chem. Soc., Chem. Commun.* **1988**, 1364. (b) Gebicki, J.; Kuberski, S.; Kaminski, R. *J. Chem. Soc., Perkin Trans. 2* **1990**, 765. (b) Irradiations were carried out with $\lambda > 300$ nm light since the $\lambda > 350$ nm light did not induce the decomposition of **8**. Under these conditions, **7**(*Z*) was decomposed to give **4** and **5**, and **4** underwent photodecarbonylation to give **5** as soon as they were formed. Thus, only **7**(*Z*) showing absorption at 2116 cm^{-1} was detected along with the absorption due to **5** and CO_2. See Figure 4b.

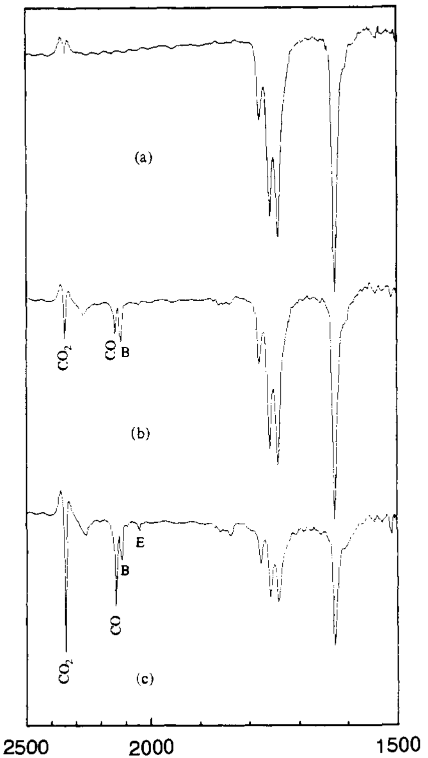
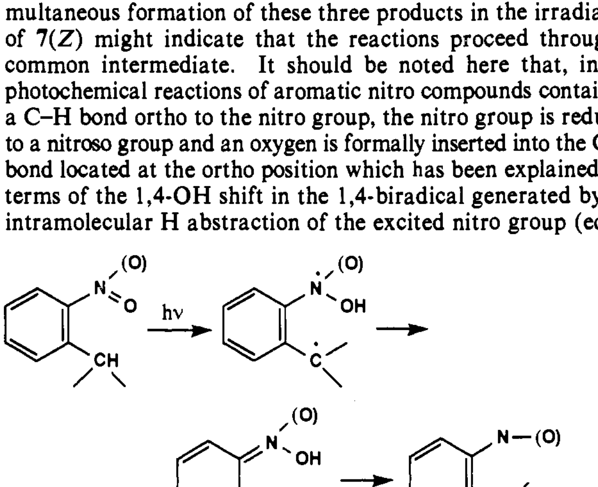


Figure 4. (a) IR spectrum of *N*-hydroxyisatin (**8**) in argon matrix at 10 K. (b) Spectrum obtained after irradiation of (a) at $\lambda > 300$ nm. (c) Spectrum obtained after irradiation of (b) at $\lambda > 254$ nm. Bands labeled B and E are assigned 7(*Z*) and **5**, respectively.

rate of reaction of the vibrational hot species. The fact that the oxime ketene 7(*E*) undergoes transformation to **4** and **5** in competition with isomerization to 7(*Z*) upon irradiation would indicate that this transformation must also go through a 1,4-biradical or related intermediates generated by photoexcitation of **7**.

Source of the Imine 5. Intervention of (2-Carboxyphenyl)nitrene. A source of **5** in the photoreaction of **3** with the >350-nm light is still puzzling at this stage. Thus, 7(*Z*) produced **5** along with **4** and 7(*E*) upon irradiation with the longer wavelength light ($\lambda > 350$ nm), which did not induce decomposition of **4** to **5**. Simultaneous formation of these three products in the irradiation of 7(*Z*) might indicate that the reactions proceed through a common intermediate. It should be noted here that, in the photochemical reactions of aromatic nitro compounds containing a C–H bond ortho to the nitro group, the nitro group is reduced to a nitroso group and an oxygen is formally inserted into the C–H bond located at the ortho position which has been explained[20] in terms of the 1,4-OH shift in the 1,4-biradical generated by the intramolecular H abstraction of the excited nitro group (eq 1).



(1)

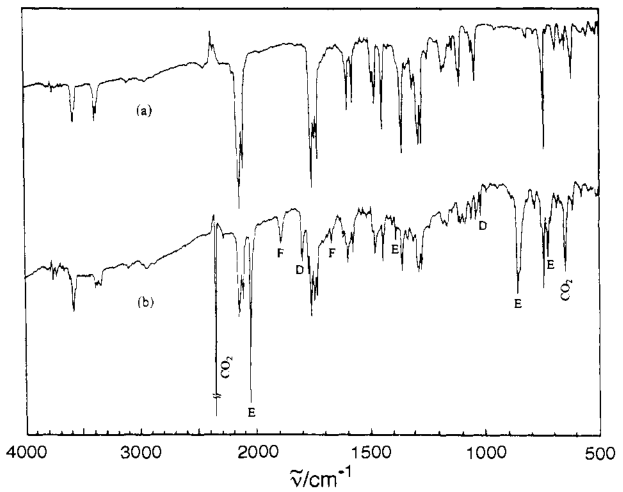


Figure 5. (a) IR spectrum of 2-carboxyphenylazide (**9**) in argon matrix at 10 K. (b) IR spectrum obtained after irradiation of (a) for 60 min at $\lambda > 350$ nm. Bands labeled D, E, and F are assigned to **4**, **5**, and **12**, respectively.

If one applies a similar mechanism to explain the photochemical transformation of *o*-nitrosobenzaldehyde (**3**) to **4a**, a formal insertion of N═O bond into the C–H bond at the ortho position, one would expect the formation of o-carboxyphenylnitrene (**10**), from which one can draw a pathway leading to **4** as well as **5**. In order to check this possibility, we prepared 2-carboxyphenylazide (**9**), a precursor for **10**, which was subjected to the photolysis. Irradiation ($\lambda > 350$ nm) of **9** in argon at 10 K resulted in a rapid disappearance of the starting materials bands and concurrent appearance of product bands in the IR (Figure 5). Comparison of the spectrum with those obtained in the photolysis of **3** immediately reveals that photomixtures contain **5** and CO_2 as a major product along with **4**. Prominent absorption bands which did not coincide with those of **4** and **5** include those at 1891 cm^{-1}, characteristic of the heterocumulenic bond, and 1747 cm^{-1}, due to the carboxy carbonyl group. These bands are assigned 3-carboxy-1-aza-1,2,4,6-cycloheptatetraene (**12**), presumably formed as a result of ring expansion[2,22] of **10**. Again careful examination of the spectral changes during irradiation of **3** producing **4** and **5** reveals the appearance of this absorption (Figure 2) suggesting nitrene (**10**) is involved in the reaction. These observations support the idea that the nitrene (**10**) is a precursor for **5** at least in the photolysis of **3** with the longer wavelength light ($\lambda > 350$ nm). Presumably, the nascent 1,4-biradical **6** generated by the intramolecular H abstraction of the excited nitroso group undergoes a 1,4-OH shift to yield the nitrene (**10**), which then abstracts H from carboxylic acid group at the ortho position to generate a 1,4-biradical (**11**) in competition with ring expansion forming the azacycloheptatetraene (**12**). The biradical (**11**) then loses CO_2 generating iminocyclohexadienylidene, a precursor for the imine (**5**), in competition with intramolecular coupling leading to **4** (Scheme IV).

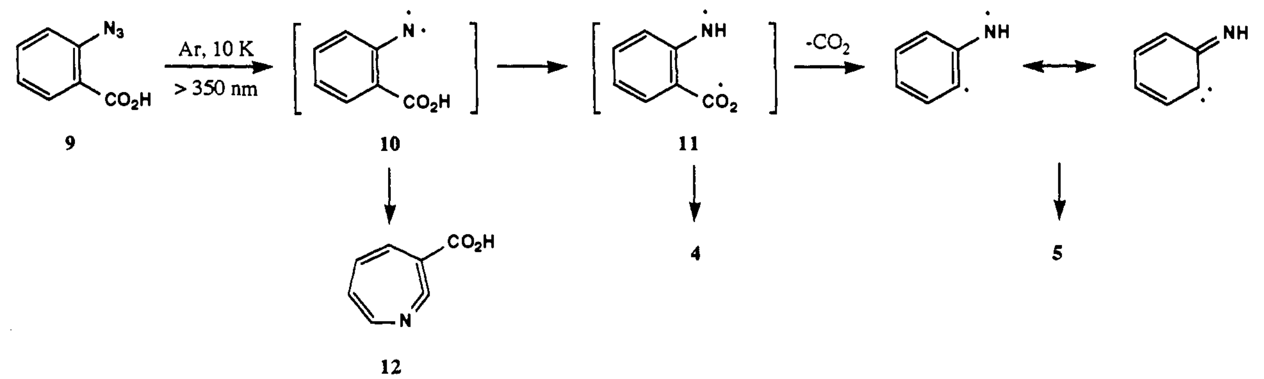
It should be noted here that the ratio of **4** to **5** obtained in the photolysis of **9** is appreciably smaller than that observed in the photolysis of **3**. This may indicate that all of the oxazolone (**4**) is not necessarily formed via **10**, some being formed directly from **6** or its excited states by a mechanism which we do not know yet. The possibility must also be considered that there should be difference in the nitrene **10** generated from **9** and **6** in terms of energies and geometries. For example, in the matrix at 10 K, the (carboxyphenyl)nitrene (**10**) must exist as two rotamers,[23] (*Z*)-**10** (nitrene N and carbonyl O cis) and (*E*)-**10** (nitrene N and carbonyl O trans), separated by a small rotational barrier, and the ratio of the two rotamers must be dependent upon the precursor structure. It is very tempting to suppose that the ratio of **4**/**5** must reflect that of *E*/*Z* in the nascent **10**. Thus, in (*Z*)-10 where the nitrenic center is located in close proximity to the carbonyl oxygen,

---

(22) Chapman, O. L.; LeRoux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 282. See, also: Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879 and references cited therein.

(23) For example, in Ar at 10 K, *o*-chlorobenzoic acid shows two IR bands in the C═O stretching region (1766 and 1744 cm^{-1}) and four bands in the OH stretching region (3571, 3562, 3548, and 3531 cm^{-1}), which is explained by two rotamers of the acid. See ref 11f.

Scheme IV

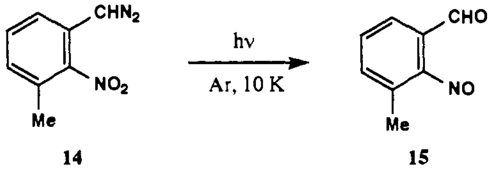


the nitrene would be trapped by the carbonyl group forming **4** via **13**, whereas the nitrene **9** in *E* conformer mainly undergoes H abstraction followed by decarboxylation forming **5** (Scheme V).

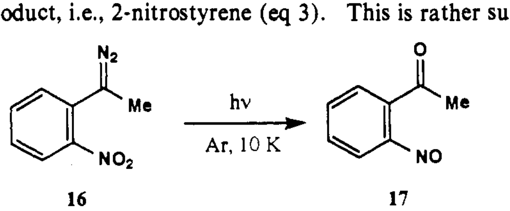
Attempts To Detect Other Possible Intermediates. The results presented above disclose the mechanism of photochemical transformation of **1** forming ultimately **4** and **5** by characterizing every key intermediate involved (Scheme VI).

The first step is considered to be oxygen atom transfer from the nitro group at the ortho position to the carbenic center. Unfortunately, however, we are not able to detect the carbene itself although its intervention is demonstrated by a trapping experiment using O_2. Nor are we able to observe intermediates expected in this oxygen migration, e.g., nitro oxonium ylide or isobenzoxazole *N*-oxide.[24] In order to know multiplicities of the carbene undergoing the migration and in a hope of observing intermediates in the reaction, we investigated the photochemical processes of the following carbene precursors having 2-nitro substituents.

First, we photolyzed 2-nitro-3-methylphenyldiazomethane (**14**) in the hope of detecting a free carbene since this diazomethane will produce phenylcarbene having the nitro group distorted out of the phenyl plane by the flanking 3-substituent and therefore the oxygen migration reaction might be slowed down. Irradiation ($\lambda > 350$ nm) of **14** in Ar matrix at 10 K, however, resulted in the formation of the corresponding nitrosobenzene (**15**, 1703 m, 1511 vw, 1417 vw, 1236 w, 1208 w, 1150 vw, 1138 w, 937 w cm^{-1}), no intermediate being detected again to the limit of our IR sensitivity (eq 2). Second, we generated 2-nitrophenylcarbene having an intramolecular reaction channel, i.e., 1,2-H migration, in order to "trap" the expected carbene intramolecularly. Thus, 1-(2-nitrophenyl)diazoethane (**16**) was photolyzed ($\lambda > 350$ nm) in Ar at 10 K, which again produced *o*-nitrosoacetophenone (**17**, 1718 s, 1703 s, 1509 vs, 1433 m, 1423 m, 1357 s, 1279 s, 1234 s, 1153 s, 1090 m, 966 w, 815 m, 768 s, 595 m, 590 m cm^{-1}) without showing any sign of absorption due to the expected "trapped" product, i.e., 2-nitrostyrene (eq 3). This is rather surprising in the light of the facts that unsubstituted 1-phenylethylidene usually undergoes a rapid 1,2-H shift producing styrene even within low-temperature matrices.[25] Recent theoretical[26] and experimental investigation[27] have indicated a nonzero barrier to the 1,2-H migration. For instance, Liu estimated the barriers for 1,2-H migration in ground-state singlet benzylchlorocarbene as 6.4 kcal/mol,[27b] while McMahon and Chapman determined a barrier in the rearrangement of triplet 1-phenylethylidene to be 4.7 kcal/mol.[25] Thus, the present observation supports the idea that oxygen shift in nitrocarbene proceeds with nearly zero activation energy.[13,14] Irradiation of methyl α-diazo-(2-nitrophenyl)acetate (**18**) also produced methyl 2-nitrosobenzoylformate (**19**, 1305 w, 1206 s, 1184 m, 1151 m, 1039 w, 1020 s, 920 w, 816 w, 808 w, 766 m) as a result of rapid oxygen transfer (eq 4), whereas similar irradiation of methyl α-diazophenylacetate gave the corresponding ketene[28] as a result the Wolff rearrangement,

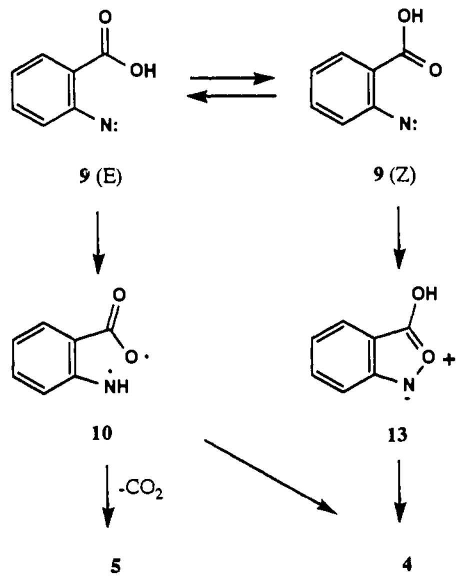


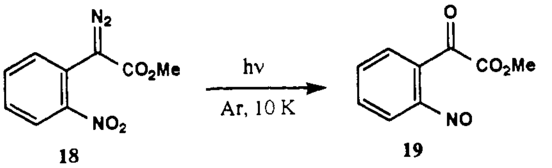
14 **15** (2)



16 **17** (3)

Scheme V





18 **19** (4)

---

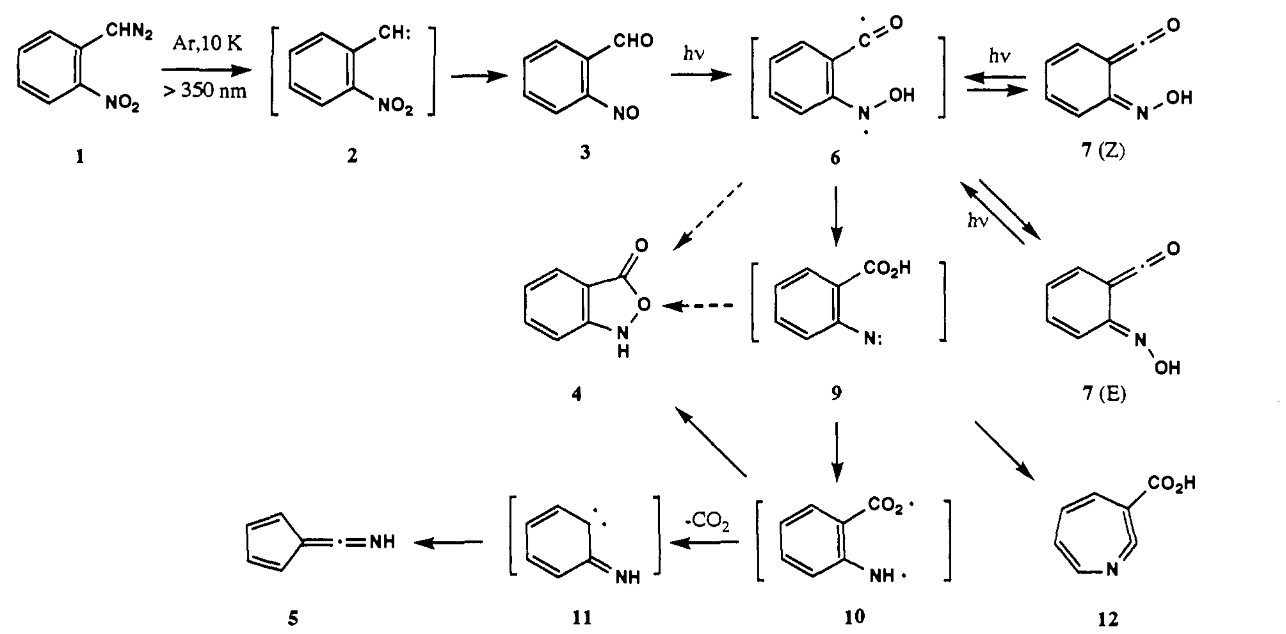
[24] We have observed benzofuroxan as an intermediate in the transformation of *o*-nitrophenylnitrene to *o*-dinitrosobenzene. Murata, S.; Tomioka, H. *Chem. Lett.* **1992**, 57.

[25] McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683.

[26] (a) Schaefer, H. F. *Acc. Chem. Res.* **1979**, *12*, 288. (b) Frenking, G.; Schmidt, J. *Tetrahedron* **1984**, *40*, 2123. (c) Raghavachari, K.; Frisch, M. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1982**, *85*, 145. (d) Altmann, J. A.; Csizmadia, I. G.; Yates, K. *J. Am. Chem. Soc.* **1974**, *96*, 4196. (e) Harding, L. B. *J. Am. Chem. Soc.* **1981**, *103*, 7469. (f) Rayez-Meaume, M. T.; Decoret, C.; Dannenberg, J. J. *Chem. Phys. Lett.* **1978**, *55*, 431.

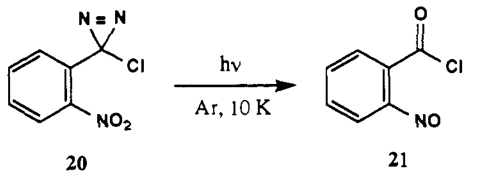
[27] (a) Su, D. T. T.; Thornton, E. R. *J. Am. Chem. Soc.* **1978**, *100*, 1872. (b) Liu, M. T. H.; Subramanian, R. *J. Phys. Chem.* **1986**, *90*, 75. (c) Liu, M. T. H. *J. Chem. Soc., Chem. Commun.* **1985**, 982.

Scheme VI



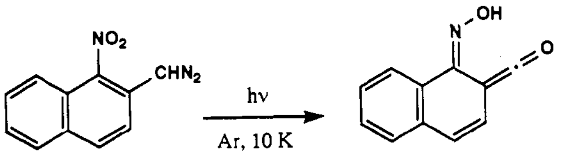
again supporting the above idea.

Since all the carbenes thus far employed in this study are considered to have potentially triplet ground states although the triplet ground state nature has not been determined yet, we then attempted to generate (2-nitrophenyl)chlorocarbene, a potential singlet ground-state carbene. Irradiation of 3-(2-nitrophenyl)-3-chlorodiazirine (**20**) in Ar at 10 K, however, again resulted in the formation of 2-nitrosobenzoyl chloride (**21**, 1801 s, 1762 w, 1517 s, 1358 m, 1310 w, 1197 s, 1153 s, 1094 m, 1082 m, 889 s, 874 s, 867 s, 830 s, 813 m, 769 s, 743 m, 648 s, 637 m cm^{-1}), no other transient absorption ascribable to either carbene or other intermediates being detected to the limit of our IR sensitivity (eq 5).



20 **21** (5)

Finally, we attempted to produce (2-nitrophenyl)carbene benzannelated so as to reduce the loss of aromaticity when the carbenic center interacts with the *o*-nitro group forming ylide or isobenzoxazole *N*-oxide in hopes of detecting an intermediate other than carbene itself. Irradiation of 2-(1-nitronaphthyl)diazomethane (**22**) designed to generate carbene along this line in Ar at 10 K, however, to our surprise, resulted in the formation of the corresponding oxime ketene (**23**, 3626 m, 2094 vs, 2074 w, 1623 w, 1573 w, 1483 w, 1420 w, 1305 w, 1218 m, 986 w, 931 m, 784 m, 769 w, 658 w, 552 w cm^{-1}); no absorptions even due to the nitrosoaldehyde were detected in this case (eq 6).



22 **23** (6)

Thus, neither carbene nor any intermediates expected in the oxygen migration are detected in any of the (2-nitrophenyl)carbenes investigated irrespective of the ground-state multiplicities and the other intramolecular reaction channels, and therefore direct information concerning the multiplicities of the carbene undergoing the migration is not obtained. Considering the extremely high efficient nature of the migration, the triplet groud state may not be responsible for this reaction. It has been noticed[2] that, in matrix photolytic experiments, reactive intermediates are not always detected, and final products are sometimes observed directly from the starting materials without showing any sign of intervention of the expected intermediates. This can be explained in terms of the intervention of vibrationally or electronically excited states of the starting materials and/or of the reactive intermediates. Presumably, the present reaction can also be interpreted by assuming one of those possible candidates.

Next step of the reaction seems to be triggered by intramolecular H abstracton by the photoexcited nitroso group. Photochemistry of nitroso compounds is not well studied compared to that of nitro compounds presumably due to the inherent labile nature. However, it has been demonstrated that 4-cyanonitrosobenzene undergoes H abstraction upon irradiation in 2-propanol solution to give the hydroxylamino radical (ArN-OH) which is characterized by ESR and is shown to lead to the hydroxylamine (ArNHOH).[29] Thus, it is conceivable to propose that *o*-nitrosobenzaldehyde (**3**) also undergoes H abstraction from the proximate formyl group even within low-temperature matrices.[30] The reaction mode of **3** appears to be very similar to that of *o*-phthaladehyde forming phthalide. Scaiano and coworkers[31] have proposed a mechanism of room-temperature photolysis of the phthaldehyde, where the phthalide arises from the singlet state reaction involving 2-hydroxyisobenzofuran as an intermediate and the triplet state reaction leading to the mixture of enols via a common biradical precursor does not seem to contribute to formation of the phthalide. The photochemistry at low temperature in matrix has been studied more recently using matrix isolation techniques by Gebicki and his co-workers,[21] who demonstrated that *o*-phthalaldehyde undergoes intramolecular H abstraction to give the mixture of enols upon irradiation ($\lambda > 313$ nm), and the enol undergoes intramolecular cyclization upon further irradiation ($\lambda > 357$ nm).

We prepared *o*-nitrophenyldiazomethane-α-d_1 and investigated its photochemistry in matrices in order to known more about the role of diazomethane hydrogen in this reaction. Overall reactions were, however, essentially the same with that of protiated **1** in terms of products. Thus, the deuterated **3**, **4**, and **5** were produced,

---

(28) Tomioka, H. unpublished observations.

(29) Levy, N.; Cohen, M. D. *J. Chem. Soc., Perkin Trans. 2* **1979**, 553.

(30) *o*-Nitrobenzaldehyde also undergoes similar H abstraction reaction from the proximate formyl group in Ar matrix at 10 K.[28]

(31) Scaiano, J. C.; Victoria, E.; George, M. V. *J. Chem. Soc., Perkin Trans. 2* **1989**, 724.

where, as was expected, shifts due to deuteration were observed. However, no new products were produced at least in detectable amounts and the ratio of **4**/**5** seemed not to change at least significantly, although a more exact analysis may detect a small difference. The only significant difference which we observed was that the photolysis of **3**-d_1 leading to **4**-d_1 and **5**-d_1 proceeded more slowly than that of the protiated **3**. Again, a more quantitative evaluation of the rate in matrix photochemistry is needed, but the apparent decrease in the rate must reflect the isotope effect in the H abstraction by the excited NO group. Thus, the deuteration did not exert the effect on the rate to the extent that it resulted in a new pathway or new intermediate.

Concluding Remarks. Finally, overall reaction indicates, in a broad sense, that *o*-nitrophenylcarbene undergoes carbene–nitrene rearrangement by a net intramolecular redox reaction. Thus, the first oxygen is transferred directly from the nitro group to the carbenic center very efficiently, presumably with nearly zero barrier. The next oxygen transfer seems not a direct mode, but might proceed stepwise, that is, by initial H transfer from the original carbenic center to the reducing center thus activating both donor and acceptor centers, followed by accepting the second oxygen in the reduced form. Carbene–nitrene rearrangement has been shown in the thermolysis of phenylazide and various precursors to the three isomeric pyridylmethylenes.[32] The low-temperature photochemical interconversion on the C_6H_5N energy surface in argon matrices studied by matrix isolation spectroscopy has confirmed that the C_6H_5N energy surface is quite slippery, and chemistry of these species is rich with carbene–carbene and carbene–nitrene rearrangements.[32] Obviously, the present rearrangement is completely different in terms of the mechanism from those thus far reported.

Experimental Section

General Methods. UV spectra were recorded on a Hitachi 220-S spectrophotometer. IR spectra were measured on a JASCO IR-700 recording spectrophotometer, and ^{1}H NMR spectra were determined with a JEOL JNM-MH-100 NMR spectrometer in CCl_4 or $CDCl_3$ with Me_4Si as an internal reference. The mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 ev). Thin-layer chromatography was done on a Merck Kieselgel 60 PF_{254}. Column chromatography was carried out on silica gel (ICN for dry column chromatography).

Matrix Isolation Spectroscopy. Matrix experiments were performed by standard techniques[33] using Iwatani Cryo Mini closed cycle helium cryostat. For IR experiments, CsI window was attached to the copper holder at the bottom of the cold head. Two opposing ports of a vacuum shroud surrounding the cold head were fitted with KBr windows for spectroscopic viewing, and the remaining parts were fitted with a quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. For the UV experiments, a sapphire cold window and quartz outer window were used. The temperature of the matrix was controlled by Iwatani TCU-1 controller (gold vs chromel thermocouple).

Argon (Seitetsu Chemicals, 99.999%), oxygen (Seitetsu Chemicals, 99.9995%), and very volatile organic compounds were mixed in a gas handling system by standard manometric techniques. Less volatile compounds were directly sublimed on the cold window, and simultaneously a large excess of host gas was deposited.

Irradiation were carried out using a Wacom 500W xenon high pressure arc lamp or a Ushio 500W mercury high pressure arc lamp. For broad-band irradiation, Toshiba cut-off filters were used (50% transmittance at the wavelengths specified).

Materials. (2-Nitrophenyl)diazomethane (1) was prepared according to the procedure of Creary.[34] Thus, 2-nitrobenzaldehyde[35] was treated with tosylhydrazine to afford the corresponding tosylhydrazone, which was reacted with sodium in ethylene glycol at 65 °C for 5 min, followed by the extraction with ethyl ether. Evaporation of the ether yielded **1** (86%) as a red oil: ^{1}H NMR (CCl)$_4$ δ 5.44 (s, 1 H), 6.88–7.76 (m, 3 H), 8.06 (d, J = 8.1 Hz, 1 H); IR (KBr) 2070, 1610, 1560, 1510, 1480, 1340, 1305, 1265 cm^{-1}.

(2-Nitrophenyl)diazomethane-α-d_1. An ethereal solution of methyl 2-nitrobenzoate (518 mg, 2.68 mmol) was added to a suspension of $LiAlD_4$ (60.0 mg, 1.43 mmol) in absolute ether (15 mL) under cooling and vigorous stirring. After usual workup, the ethereal extract was chromatographed on silica gel column eluted with $CHCl_3$ to obtain 2-nitrobenzyl-α,α-d_2 alcohol as a brown solid in 42.9% yield: mp 68–70 °C; ^{1}H NMR ($CDCl_3$) δ 2.64 (brs, 1 H9, 7.13–7.80 (m, 3 H), 7.96 (d, J = 8.2 Hz, 1 H); MS (rel intensity) 136 (8), 92 (40), 78 (100).

The nitroalcohol (190 mg, 1.23 mmol) was oxidized with pyridinium chlorochromate[36] (396 mg, 1.84 mmol) in CH_2Cl_2. Usual workup, followed by chromatography on silica gel column eluted with $CHCl_3$–*n*-hexane (1:1) gave 2-nitrobenzaldehyde-α-d_1 (>99% d) in 75.1%: mp 39–40 °C; ^{1}H NMR ($CDCl_3$) δ 7.66–8.19 (m, 4 H); IR (KBr disc) 1680, 1530, 1350 cm^{-1}; MS (rel intensity) 123 (8), 122 (100), 94 (63), 66 (85).

The nitroaldehyde (32 mg, 0.1 mmol) was diazotized according to the procedure described above for **1** to give (2-nitrophenyl)diazomethane-α-d_1 as a red oil: ^{1}H NMR (CCl_4) δ 6.90–7.54 (m, 3 H), 8.10 (d, J = 8.2 Hz, 1 H); IR (NaCl, neat) 2070, 1515, 1500, 1335, 1290, 1260 cm^{-1}.

(4-*n*-Butyl-2-nitrophenyl)diazomethane (1b). To a solution of 4-*n*-butylacetanilide (1.50 g, 7.84 mmol) in acetic acid (10 mL) was added nitric acid (69%, 1.5 mL) dropwise at such a rate that the temperature did not rise above 10 °C. The mixtures were stirred for 1 h at room temperature and poured into ice–water (200 mL) to give 4-*n*-butyl-2-nitroacetanilide (1.82 g, 98.3%) as yellow needles: mp 66–67 °C; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 8.2 Hz, 3 H), 1.17–1.76 (m, 4 H), 2.24 (s, 3 H) 2.62 (t, J = 8.2 Hz, 2 H), 7.36 (dd, J = 8.3 and 3.2 Hz, 1 H), 7.89 (d, J = 3.2 Hz, 1 H), 8.50 (d, J = 8.3 Hz, 1 H), 10.03 (brs, 1 H); IR (KBr disc), 3370, 1710, 1515, 1340 cm^{-1}.

A mixture of nitroacetanilide (1.79 g, 7.58 mmol), concentrated HCl (15 mL), and H_2O (15 mL) was refluxed for 17 h. Extraction with ether, drying, evaporation of the solvent, and distillation afforded 4-*n*-butyl-2-nitroaniline as a reddish liquid (1.15 g, 78.9%): bp 110–125 °C/0.7 Torr; ^{1}H NMR (CCl_4) δ 0.94 (t, J = 8.2 Hz, 3 H), 1.16–1.75 (m, 4 H), 2.50 (t, J = 8.2 Hz, 2 H), 5.83 (brs, 2 H), 6.60 (d, J = 8.1 Hz, 1 H), 7.04 (dd, J = 8.1 and 3.2 Hz, 1 H), 7.76 (d, J = 3.2 Hz, 1 H).

To a stirred solution of the nitroaniline (1.14 g, 5.92 mmol) in dioxane (1.2 mL) and concentrated HCl (1.36 mL) cooled with ice–water was added a solution of $NaNO_2$ (0.412 g, 5.92 mmol) in H_2O (0.57 mL) dropwise. The resulting diazonium mixture solution was brought to pH 5.0 by adding aqueous NaOAc solution and was added to a mixture of 10% formaldoxime solution [prepared[37] by heating paraformaldehyde (0.273 g, 9.10 mmol), NH_2OHHCl (0.632 g, 9.10 mmol) and H_2O (4 mL) followed by addition of NaOAc (1.22 g, 8.97 mmol), $CuSO_4$ (0.299 g, 1.20 mmol), sodium sulfite (24 mg), NaOAc (3.95 g) and H_2O (4.3 mL)]. After stirring for 1 h, the mixtures were made acidic by the addition of HCl, extracted with ether and the ether was evaporated to give a red oil, which was dissolved in dioxane (2 mL) and added to a solution of ammonium iron(II) sulfate (7.18 g) in H_2O (12 mL). The mixture was refluxed for 4 h and extracted with ether. After washing with 1 N Na_2CO_3, drying with Na_2SO_4, and evaporation of the solvent, the residue was chromatographed [silica gel column, $CHCl_3$–*n*-hexane (1:3)] to give 4-*n*-butyl-2-nitrobenzaldehyde as a red liquid (31.8%): ^{1}H NMR (CCl_4) δ 0.97 (t, J = 8.2 Hz, 3 H), 1.21–1.87 (m, 4 H), 2.76 (t, J = 8.2 Hz, 2 H), 7.46 (dd, J = 8.2 and 2.1 Hz, 1 H), 7.72–7.89 (m, 2 H), 10.22 (s, 1 H); IR (NaCl neat) 1700, 1530, 1350 cm^{-1}; MS (rel intensity) 207 (M^+, 4), 177 (100), 134 (45).

The nitrobenzaldehyde was converted to the corresponding diazomethane (**1b**) by a similar procedure to that described for **1** to obtain an orange oil (80.3%): ^{1}H NMR (CCl_4) δ 0.92 (t, J = 8.2 Hz, 3 H), 1.16–1.76 (m, 4 H), 2.61 (t, J = 8.2 Hz, 2 H), 6.42 (s, 1 H), 6.95 (d, J = 8.1 Hz, 1 H), 7.32 (dd, J = 8.2 and 2.1 Hz, 1 H), 7.94 (d, J = 2.1 Hz, 1 H); IR (NaCl neat) 2070, 1550, 1515, 1335, 1270 cm^{-1}.

(2-Nitro-3-methylphenyl)diazomethane (14) was prepared by treating 2-nitro-3-methylbenzaldehyde[38] with tosylhydrazine, followed by heating the resulting hydrazone in Na/ethylene glycol at 65 °C for 5 min as an orange oil, 65%: ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3 H), 5.16 (s, 1 H), 6.72–6.92 (m, 2 H), 7.16–7.36 (m, 1 H); IR (KBr) 2027, 1600, 1520, 1355, 852, 772 cm^{-1}.

1-(2-Nitrophenyl)diazoethane (16) was prepared by the oxidation of the corresponding hydrazone with MnO_2 by the method of Trentham et al.[39]

---

(32) (a) Crow, W. D.; Wentrup, C. *Tetrahedron Lett.* **1968**, 6149. (b) Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1969**, 1386. (c) Crow, W. D.; Paddon-Row, M. N. *Tetrahedron Lett.* **1972**, 2231. (d) Crow, W. D.; Paddon-Row, M. N.; Sutherland, D. S. *Tetrahedron Lett.* **1972**, 2239. (e) Thetaz, C.; Wentrup, C. *J. Am. Chem. Soc.* **1976**, *98*, 1258. (f) Crow, W. D.; Khan, A. N.; Paddon-Row, M. N. *Aust. J. Chem.* **1975**, *28*, 1741, 1755, 1763. (g) Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *Recl. Trav. Chem. Pays-Bas.* **1979**, *98*, 334.

(33) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 7597.

(34) Creary, X. *Organic Synthesis*; Wiley: New York, **1985**, *64*, 207.

(35) Kalir, A. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p825.

(36) (a) Choi, H. S.; Kuczkowski, R. L. *J. Org. Chem.* **1985**, *50*, 901. (b) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, *31*, 2647.

(37) Beech, W. F. *J. Chem. Soc.* **1954**, 1297.

(38) Mayer, F. *Chem. Ber.* **1914**, *47*, 406.

Methyl α-diazo-2-nitrophenylacetate (18) was obtained by adding tosyl azide (400 mg, 2.05 mmol) to a mixture of methyl 2-nitrophenylacetate (400 mg, 2.05 mmol) and KF–Al_2O_3[40] (420 mg, 2.05 mmol) in MeCN (6 mL), followed by usual workup, as an orange solid (350 mg, 77.2%): mp 69–72 °C; ^{1}H NMR (CCl_4) δ 3.78 (s, 3 H), 7.30–7.62 (m, 3 H), 7.96 (d, J = 8.1 Hz, 1 H); IR (KBr disc) 2110, 1715, 1690, 1530, 1370 cm^{-1}.

3-(2-Nitrophenyl)-3-chlorodiazirine (20). A mixture of 2-nitrobenzonitrile (2.22 g, 15.0 mmol), $AlCl_3$ (2.0 g, 15.0 mmol), and urea (14.4 g) was heated at 200 °C for 2 h. To the cooled mixture, hot water (20 mL) was poured, and the solution was then poured onto 5 N NaOH aqueous solution (40 mL), which was extracted with $CHCl_3$. Evaporation of the solvent left brown residue, which was dissolved in EtOH. Addition of picric acid to the solution, followed by cooling for 3 days produced 2-nitrobenzamidine picrate[41] as a yellow solid (0.51 g, 8.6%). To a solution of picrate (300 mg) and NaLi (185 mg) in DMSO (3.1 mL)–*n*-hexane (2.4 mL) was added NaOCl aqueous solution (3 mL) containing NaCl (525 mg) under cooling and vigorous stirring. After stirring for 30 min at 10 °C, the mixture was extracted with hexane. Preparative TLC (silica gel) with $CHCl_3$–*n*-hexane (1:20) of the extract provided the desired diazirine (11 mg, 8.0%); ^{1}H NMR (CCl_4) δ 7.52–7.70 (m, 3 H), 7.98–8.12 (m, 1 H); IR (NaCl neat) 1570, 1530, 1350 cm^{-1}.

2-(1-Nitronaphthyl)diazomethane (22) was prepared by stirring NaH and tosylhydrazone of 1-nitro-2-naphthaldehyde[42] in anhydrous THF for 15 min at room temperature followed by usual workup and TLC as an orange solid in 39% yield; mp 73.0 °C (dec); ^{1}H NMR ($CDCl_3$) δ 5.52 (s, 1 H), 7.00–8.00 (m, 6 H); IR (KBr) 2070, 1502, 1405, 1341, 1320, 808, 741 cm^{-1}.

o-**Nitrosobenzaldehyde (3)** was prepared by heating *trans*-2,2′-diformylazobenzene dioxide.[9] **2,1-Benzisoxazolone (4)** was obtained by the treatment of (*o*-hydroxylamino)-*N*,*N*-dimethylbenzamide with aqueous alkaline solution.[15] **Carbonylcylcopentadiene imine (5)** was generated by the photolysis of benzotriazole.[16] *o*-**Azidobenzoic acid (8)** was obtained by treatment of antranilic acid with HCl/$NaNO_2$ followed by NaN_3.[43] *N*-Hydroxyisatin was prepared[44] by the reaction of 2-nitrobenzoyl chloride with CH_2N_2. All other chemicals were used as received or distilled before use as specified.

Acknowledgment. The authors thank Professors J. Gebicki (Technical University, Lods), K. Nakasuji (Institute for Molecular Science, Okazaki), and S. Murata (Mie University) for their stimulating discussions. The present work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan which is gratefully acknowledged.

---

(39) Walker, J. W.; Reid, G. P.; McCray, J. A.; Trentham, D. R. *J. Am. Chem. Soc.* **1988**, *110*, 1970.

(40) Yamasaki, J.; Ando, T. *Chem. Lett.* **1979**, 755.

(41) Short, W. F.; Purtridge, M. W. U.S., 2456386 (1948); *Chem. Abstr.* **1949**, *43*, 3456.

(42) Makosza, M.; Owczarczyk, Z. *J. Org. Chem.* **1989**, *54*, 5094.

(43) Maffei, S.; Coda, L. *Gazz. Chem. Ital.* **1955**, *85*, 1300.

(44) Taylor, E. C.; Eckroth, D. D. *Tetrahedron* **1964**, *20*, 2059.

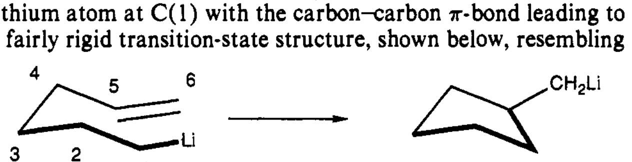
Highly Stereoselective Tandem Cyclizations of 5-Hexenyllithiums: Preparation of Endo-2-Substituted Bicyclo[2.2.1]heptanes and 3-Substituted *trans*-Bicyclo[3.3.0]octanes

William F. Bailey,* Atmaram D. Khanolkar, and Kaustubh V. Gavaskar

Contribution from the Department of Chemistry, The University of Connecticut, Storrs, Connecticut 06269-3060. *Received May 1, 1992*

Abstract: Tandem cyclization of diolefinic alkyllithiums, derived from acyclic diolefinic alkyl iodides by low-temperature lithium–iodine exchange, proceeds via two highly stereoselective and totally regiospecific 5-*exo-trig* ring closures to deliver bicyclic alkyllithiums. Trapping of the organolithium product by addition of an electrophile cleanly affords functionalized bicyclic molecules in good yield. In this way both endo-2-substituted bicyclo[2.2.1]heptanes and 3-substituted *trans*-bicyclo[3.3.0]octanes have been prepared in isolated yields of 65–80% from the readily available 3-(2-iodoethyl)-1,5-hexadiene (**5**) and 7-iodo-4-ethenyl-1-heptene (**9**), respectively. Attempts to effect tandem cyclization of 5,10-undecadienyllithium (**11**), which would be mediated by a secondary alkyllithium species, were unsuccessful. The results suggest that tandem anionic cyclization provides a convenient route to a variety of bicyclic systems not readily available by other approaches.

The isomerization of 5-hexenyllithiums has attracted the attention of a number of groups as a route to functionalized cyclopentylmethyl-containing products.[1,2] We have recently demonstrated that such cyclizations involving monosubstituted 5-hexenyllithiums are highly stereoselective and totally regiospecific 5-*exo-trig* processes.[3] Molecular orbital calculations indicate that the high degree of stereocontrol inherent in these cyclizations is a consequence of an energetically favorable coordination of the lithium atom at C(1) with the carbon–carbon π-bond leading to a fairly rigid transition-state structure, shown below, resembling a chair cyclohexane in which a substituent preferentially occupies a pseudoequatorial position.



This recently acquired ability to predict the stereochemical outcome of isomerization of a substituted 5-hexenyllithium,

---

(1) (a) Smith, M. J.; Wilson, S. E. *Tetrahedron Lett.* **1981**, *22*, 4615. (b) Ross, G. A.; Koppang, M. D.; Bartak, D. E.; Woolsey, N. F. *J. Am. Chem. Soc.* **1985**, *107*, 6742. (c) Cooke, M. P., Jr. *J. Org. Chem.* **1992**, *57*, 1495 and references therein. (d) Chamberlin, A. R.; Bloom, S. H.; Cervini, L. A.; Fotsch, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 4788 and references therein. (e) Broka, C. A.; Shen, T. *J. Am. Chem. Soc.* **1989**, *111*, 2981. (f) Paquette, L. A.; Gilday, J. P.; Maynard, G. D. *J. Org. Chem.* **1989**, *54*, 5044. (g) Krief, A.; Barbeaux, P. *Synlett* **1990**, 511.

(2) Bailey, W. F.; Patricia, J. J.; DelGobbo, V. C.; Jarret, R. M.; Okarma, P. J. *J. Org. Chem.* **1985**, *50*, 1999. (b) Bailey, W. F.; Nurmi, T. T.; Patricia, J. J.; Wang, W. *J. Am. Chem. Soc.* **1987**, *109*, 2442. (c) Bailey, W. F.; Khanolkar, A. D. *J. Org. Chem.* **1990**, *55*, 6058. (d) Bailey, W. F.; Khanolkar, A. D. *Tetrahedron* **1991**, *47*, 7727.

(3) Bailey, W. F.; Khanolkar, A. D.; Gavaskar, K.; Ovaska, T. V.; Rossi, K.; Thiel, Y.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 5720.