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Photochemistry of 2-(Methoxycarbonyl)phenyl Azide Studied by Matrix-Isolation Spectroscopy. A New Slippery Energy Surface for Phenylnitrene

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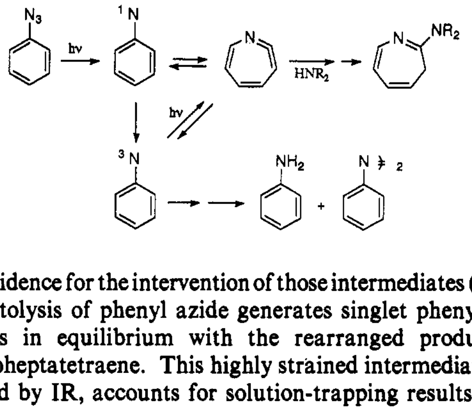
Abstract: Broad-band irradiation ($\lambda > 350$ nm) of 2-(methoxycarbonyl)phenyl azide (**1**) in Ar at 10 K monitored by IR and UV–vis spectroscopy resulted in the formation of at least five major products, all of which were shown to be photointerconvertible under these conditions. The two products showing intact methoxycarbonyl carbonyl stretching absorption bands were assigned as (2-(methoxycarbonyl)phenyl)nitrene (**2**) and 3-(methoxycarbonyl)-1,2,4,6-azacycloheptatetraene (**3**), probably formed as a result of ring expansion of **2**, while the products showing sharp absorption bands at 2118 and 2088 cm^{-1} due to ketene functional groups were assigned to the geometrical mixture of carbonyl oximino benzenes **16**, presumably formed by formal 1,4-methoxy migration in **2**, and the one showing carbonyl absorption at 1857 cm^{-1} was assigned as *N*-methoxyazetinone **15**, produced as a result of photocyclization of **16**. These assignments were unequivocally verified by generating the same reaction mixtures by photodecarbonylation of *N*-methoxyisatin (**23**) in an argon matrix at 10 K. That phenylnitrene–pyridylmethylene interconversions were not attained once the 2-methoxycarbonyl group was introduced was also shown.

Photochemistry of phenyl azides has attracted continued and ever increasing interests[1] in view of the useful applications in heterocyclic syntheses,[1] in photoresist technologies,[1,2] and in the biochemical method of photoaffinity labeling,[1,3,4] and the complete picture of the chemical reactions initiated by the elimination of molecular nitrogen has began to unfold recently. Thus, preparative study has gradually revealed various chemical paths that require the involvement of different intermediates and matrix isolation,[5,6] and, also, flash-photolytic investigation[7] has provided direct evidence for the intervention of those intermediates (Scheme I). Photolysis of phenyl azide generates singlet phenylnitrene which is in equilibrium with the rearranged product, i.e., azacycloheptatetraene. This highly strained intermediate, characterized by IR, accounts for solution-trapping results, giving, for example, 2-amino-3*H*-azepine in the presence of amine. The singlet nitrene undergoes intersystem crossing to the triplet, again characterized by spectroscopic means, which either produces azobenzene by dimerization or affords aniline by abstracting hydrogen from the solvent in fluid solution. The triplet nitrene, on the other hand, is shown to undergo ring expansion upon photoexcitation within the matrix.

Scheme I



Chemistry for phenylnitrenes having functional groups at the ortho position has been recognized and employed as very useful routes to the nitrogen heterocycles,[1,8] since those nitrenes usually interact with the proximate functional group to produce an important class of azacyclic compounds which are otherwise difficult to obtain. However, spectroscopic studies to detect and characterize the intermediates involved in these intramolecular reactions are relatively scant, and thus, it is of immediate interest to know how those intermediates proposed in the chemistry of "simple" phenylnitrenes are trapped by the proximate functional groups. For instance, we[9] and others[10] have provided spectroscopic evidence, using matrix-isolation techniques, that, in the photolysis of 2-nitrophenyl azide forming benzofuroxan, 2-bis(nitroso)-

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(1) (a) *Azides and Nitrenes, Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984. (b) Nitrenes; Lwowski, W., Ed.; Interscience: New York, 1970. (c) Iddon, B.; Meth-Cohn, O.; Scriven, E. F. V.; Suschitzky, H.; Gallagher, P. T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 900. (d) Scriven, E. F. V. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1981; Vol. 2, Chapter 1. (e) Lwowski, W. In *Reactive Intermediates*; Jones, M., Moss, R. A., Ed.; Wiley: New York, 1981; Chapter 8.

(2) (a) Meijer, E. W.; Nijhuis, S.; van Vroonhoven, F. C. B. M. *J. Am. Chem. Soc.* **1988**, *110*, 7209. (b) Yan, M.; Cai, S. X.; Wybourne, M. N.; Keana, J. F. W. *Ibid.* **1993**, *115*, 814.

(3) (a) Kanakarajan, K.; Goodrich, R.; Young, M. J. T.; Soundararajan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6536. (b) Shaffer, N. W.; Platz, M. S. *Tetrahedron Lett.* **1989**, *30*, 6465. (c) Soundararajan, N.; Platz, M. S. *J. Org. Chem.* **1990**, *55*, 2034. (d) Platz, M. S.; Watt, D. S. *Photochem. Photobiol.* **1991**, *54*, 329. (e) Cai, S. X.; Keana, J. F. W. *Tetrahedron Lett.* **1989**, *30*, 5409. (f) Keana, J. F. W.; Cai, S. X.; *J. Org. Chem.* **1990**, *55*, 3640.

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(5) (a) Chapman, O. L.; Le Roux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 282. (b) Chapman, O. L.; Sheridan, R. S. *Ibid.* **1979**, *101*, 3690. (c) Dunkin, I. R.; Tompson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1980**, 499. (d) Dunkin, I. R.; Thompson, P. C. P. *Ibid.* **1982**, 1192. (e) Dunkin, I. R.; Donelly, T.; Lockhart, T. S. *Tetrahedron Lett.* **1985**, 359. (f) Wentrup, C.; Winter, H. W. *J. Am. Chem. Soc.* **1980**, *102*, 6159. (g) Wentrup, C.; Thètaz, C.; Tagliaferri, E.; Linder, H. J.; Kitscke, B.; Winter, H. W.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 566. (h) Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879.

(6) (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.

(7) (a) Sundberg, R. J.; Heintzelman, R. W. *J. Org. Chem.* **1974**, *39*, 2546. (b) Degraff, B. A.; Gillespie, D. W.; Sundberg, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 7491. (c) Sumitani, M.; Nagakura, S.; Yoshihara, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2995. (d) Nielsen, P. E.; Buchard, O. *Photochem. Photobiol.* **1982**, *35*, 317. (e) Shields, C. J.; Chrisope, D. R.; Schuster, G. B.; Dixon, A. J.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 4723. (f) Li, Y. Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *Ibid.* **1988**, *110*, 8092. (g) Schrock, A. K.; Schuster, G. B. *Ibid.* **1984**, *106*, 5234, 5229. (h) Liang, T.-Y.; Schuster, G. B. *Ibid.* **1987**, *109*, 7803. (i) Albini, A.; Bettinetti, G.; Minoli, G. *Ibid.* **1991**, *113*, 6928.

(8) Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, *28*, 279.

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(10) (a) Dunkin, I. R.; Lynch, M. A.; Boulton, A. J.; Henderson, N. *J. Chem. Soc., Chem. Commun.* **1991**, 1178. (b) Hacker, N. P. *J. Org. Chem.* **1991**, *56*, 5217.

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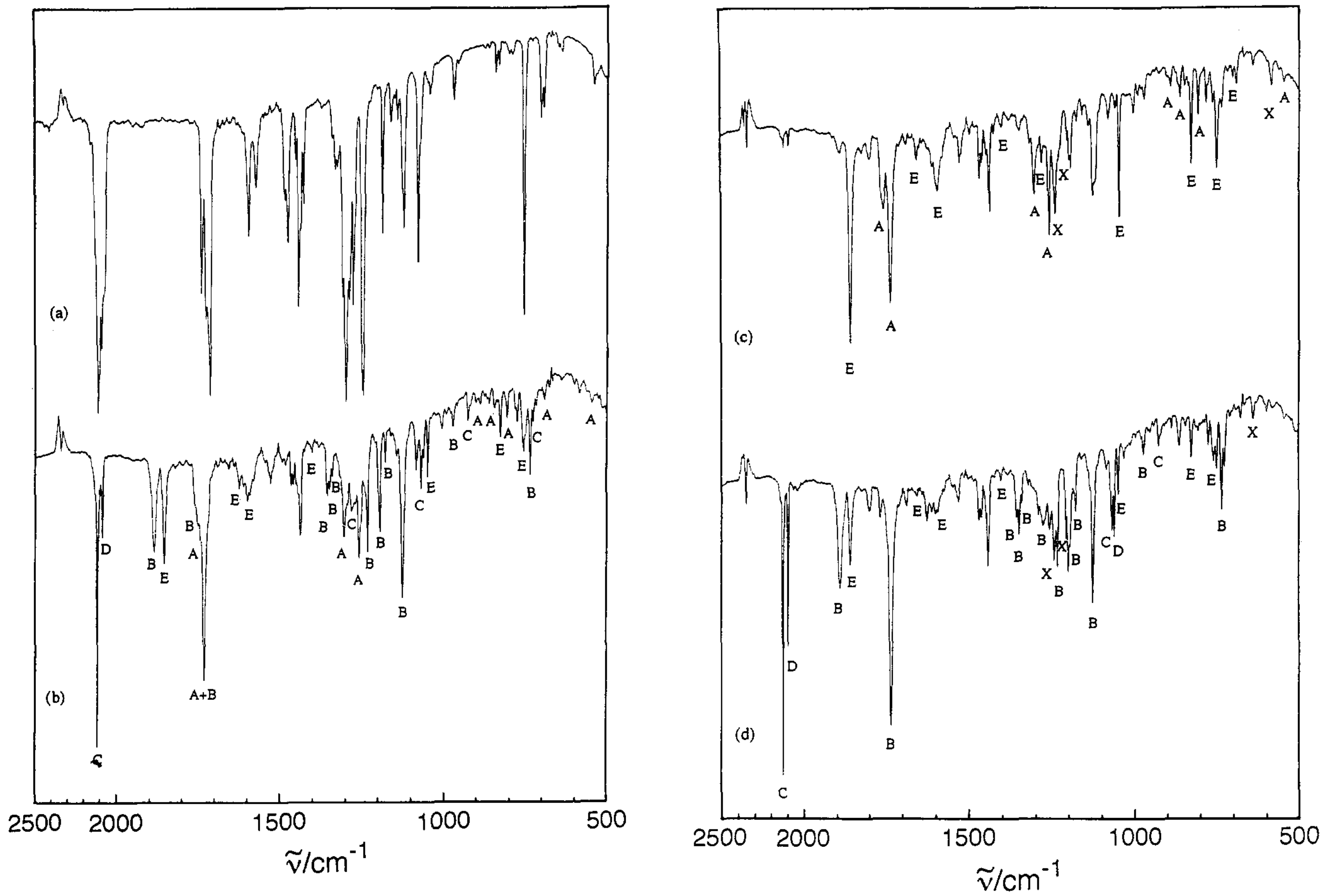
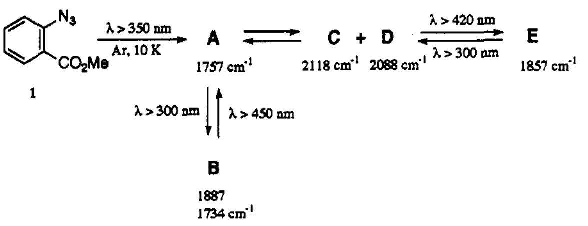


Figure 1. (a) IR spectrum of methyl *o*-azidobenzoate (**1**) in an Ar matrix at 10 K. (b) IR spectrum obtained after irradiation of **1** for 16 h at λ > 350 nm. (c) IR spectrum obtained after irradiation of (b) at λ > 420 nm for 2 h 54 min. (d) Spectrum obtained after irradiation of (c) at λ > 300 nm for 36 min.

benzene, which has been proposed[11] in the photointerconversion of benzofuroxan, is actually produced. As an extension of such a study, we investigated the photochemistry of 2-(methoxycarbonyl)phenyl azide in an argon matrix at cryogenic temperature and found that, although (2-(methoxycarbonyl)phenyl)nitrene undergoes ring expansion to form 3-(methoxycarbonyl)-1,2,4,6-azacycloheptatetraene, it also undergoes unusual formal 1,4-methoxy migration to generate carbonyl oximino benzenes, which then undergo cyclization to afford azetinone and that all of those five products were in photoequilibrium under matrix conditions.

Results and Discussion

Deposition of 2-(methoxycarbonyl)phenyl azide (**1**) in an argon matrix at 20 K gave the IR and UV–vis spectrum shown in Figures 1a and 2a, respectively. Broad-band irradiation (16 h, λ > 350 nm) of the sample cooled to 10 K resulted in a decrease in starting material bands and a concurrent appearance of new bands in the IR (Figure 1b). The matrix also took on a distinct yellow hue during the irradiation. In the UV–vis spectra, the disappearance of the azide spectrum and the formation of a broad band with a maximum at around 450 nm were observed (Figure 2b). Careful analysis of these product absorption bands by plotting their intensities as a function of the irradiation time and wavelength of light suggested that there were at least five major photoproducts; they are **A** (1757 w, 1734 m, 1305 w, 889 w, 805 w, 689 w, and 583 w cm^{-1}), **B** (1887 m, 1734 m, 1356 w, 1349 w, 1342 w, 12772, 1231 m, 1194 m, 1176 w, 1125 m, 969 w, and 734 m cm^{-1}), **C** (2118 s, 1067 m, 925 w, 845 w, and 725 w cm^{-1}), **D** (2088 s and 1061 m cm^{-1}), and **E** (1857 s, 1656 m, 1593 m, 1404 w, 1282 w, 1048 m, 826 m, 784 m, and 700 w cm^{-1}). Control experiments showed that all of those products were interconvertible upon irradiations (eq 1). Thus, irradiation of the initial photomixtures



(1)

containing all the major photoproducts with light at λ > 420 nm resulted in the disappearance of the absorption bands ascribable to **B**, **C**, and **D** and in the concurrent growth of the bands due to **A** and **E** (Figure 1c). Simultaneously, the color in the matrix was bleached; the visible absorption of the initial product disappeared (Figure 2c). Irradiation of the mixture containing **A** and **E** with light of λ > 300 nm then reproduced the IR bands ascribable to **B**, **C**, and **D** (Figure 1d), and the matrix took on a yellow hue again (Figure 2d).

What are those photoproducts (**A**–**E**)? Analysis of the major IR bands provided some insights into their structures. First, the presence of the intense 1887-cm^{-1} band in **B** suggested the presence of a strained heterocumulene bond, indicating an aza-1,2,4,6-cycloheptatetraene structure for **B**. Only a slight shift of the C=O stretching absorption band in going from **1** to **B**, then, suggested that the methoxycarbonyl group was intact during this transformation. Thus, 3-(methoxycarbonyl)-1,2,4,6-azacycloheptatetraene (**3**) was proposed as the most probable structure for **B**, which must be formed by loss of nitrogen from **1** followed

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[11] Calzaferri, G.; Gleiter, R.; Knauer, K.-H.; Martin, H.-D.; Schmidt, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 86.

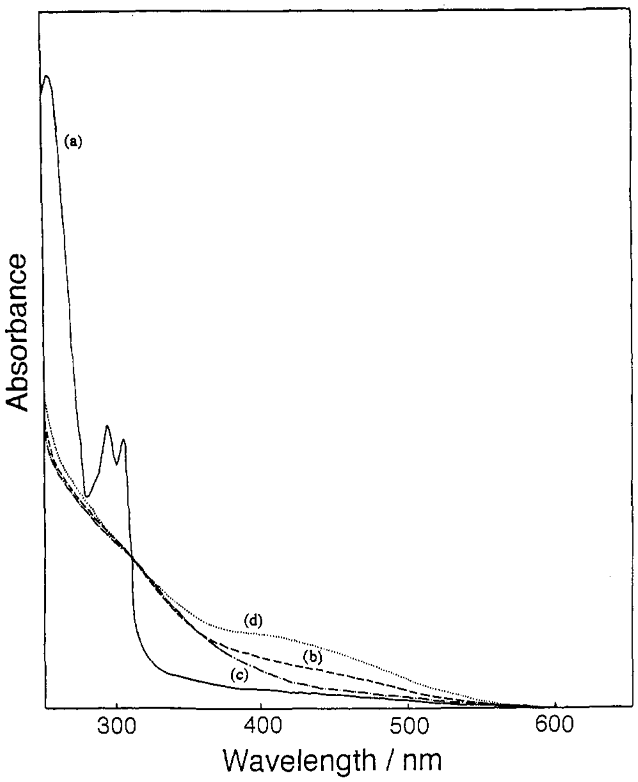
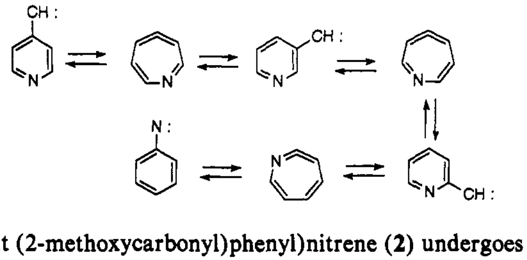


Figure 2. (a) UV spectrum of **1** in an Ar matrix at 10 K. (b) Spectrum obtained after irradiation of **1** for 17 h at λ > 350 nm. (c) Spectrum obtained after irradiation of (b) at λ > 420 nm for 18 min. (d) Spectrum obtained after irradiation of (c) at λ > 350 ± 20 nm for 1 h.

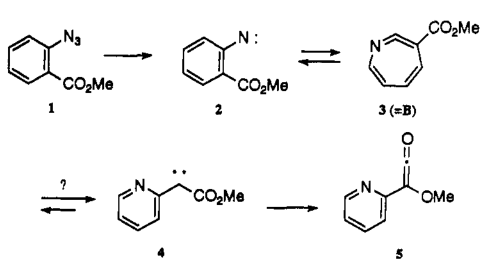
by ring expansion. The methoxycarbonyl group was not intact, on the other hand, during the formation of **C**–**E**. Thus, strong, sharp absorptions appearing at 2118 and 2088 cm^{-1} in **C** and **D**, respectively, with loss of the carbonyl band suggested that the carbonyl group should be transformed into ketene groups in these products, while a considerably shifted C═O stretching absorption (1856 cm^{-1}) in **E**, compared to that in **1** and **B**, suggested that the methoxycarbonyl group should be changed to the other carbonyl function as a result of structural reorganization.

The photochemical interconvertible nature including phenylnitrene and azacycloheptatetraene in the present reaction systems is strongly reminiscent of the studies by Chapman and his co-workers[5,12] who have demonstrated that phenylnitrene and isomeric pyridylmethylenes are photointerconvertible within matrices. For example, irradiation (λ > 200 nm) of a 4-(diazomethyl)pyridine matrix isolated in Ar at 12 K gives triplet 4-pyridylmethylene, which, upon further irradiation, isomerizes to give 3-pyridylmethylene, 2-pyridylmethylene, and phenylnitrene via the isomeric azacycloheptatetraenes, the isomeric compositions being dependent upon the wavelength of light irradiated (eq 2). It might be possible, based on these observations,



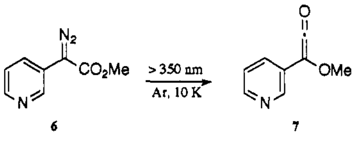
(2)[12]

that (2-methoxycarbonyl)phenyl)nitrene (**2**) undergoes isomerization, presumably via azacycloheptateraene **3** ≡ **B**, to give pyridyl(methoxycarbonyl)carbenes (e.g., **4**) which then undergo the Wolff rearrangement to produce ketene derivatives (e.g., **5**) (eq 3). In order to check this possibility, we prepared the



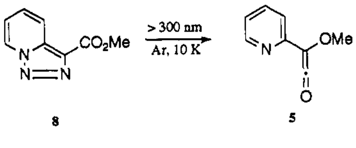
(3)

precursors for their expected pyridylcarbenes and investigated the photochemistry within matrices. Irradiation (λ > 350 nm) of methyl α-diazo-3-pyridylacetate (**6**, 2094 vs, 1721 s, 1486 s, 1441 s, 1364 s, 1266 s, 1196 s, 1162 s, 1067 s, 1035 m, 804 m, and 707 m cm^{-1}) matrix-isolated in Ar at 10 K resulted in the simultaneous disappearance of the diazo (2094 cm^{-1}) and carbonyl bands (1721 cm^{-2}) and concurrent appearance of new bands (2124 vs, 1706 m, 1592 w, 1572 w, 1496 w, 1482 m, 1441 m, 1167 w, 942 w, 905 w, and 708 m cm^{-1}) in the IR, which was easily assigned to ketene **7**, especially on the basis of a strong, sharp band at 2124 cm^{-1} (eq 4). However, not only the ketene absorption



(4)

band but also all the other prominent bands observed for **7** did not coincide with any of those formed in the photolysis of **1**. Moreover, extended irradiation of the photoproduct with the light of different wavelengths (i.e., λ > 420, 350, > 300, and > 250 nm) did not cause any appreciable change in the spectra, indicating that the photoproduct has no interconvertible nature. Essentially similar observations were seen in the photolysis of 3-(methoxycarbonyl)-*v*-triazolo[3,4-*a*]pyridine (**8**, 1717 s, 1530 m, 1526 m, 1452 m, 1270 m, 1255 m, 1228 s, 1072 s, 792 w, and 751 m cm^{-1}), where none of the prominent absorption bands of ketene (**5**, 2124 s, 2104 s, 1660 m, 1441 w, 1384 w, 1284 w, 1276 w, 1217 m, 1130 w, and 775 w cm^{-1}) produced matched with those of **C** or **D** and the ketene did not undergo any photochemical transformation (eq 5). These control experiments clearly demonstrate that (2-(methoxycarbonyl)phenyl)nitrene–(methoxycarbonyl)pyridyl)carbene rearrangement (e.g., **2** → **4**) is not attained.



(5)

Another possibility which should be considered in this special nitrene system must be the intramolecular interaction between the nitrenic center and methoxycarbonyl group at the ortho position. In the chemistry of phenylcarbenes, carbenes bearing functional groups at the ortho position usually produce the product as a result of the intramolecular interaction between the carbenic center and the ortho substituents. Thus, *o*-tolymethylene generated in an Ar matrix produces *o*-xylylene as a result of a 1,4-H shift.[13] We[14] have demonstrated, on the other hand, that (*o*-

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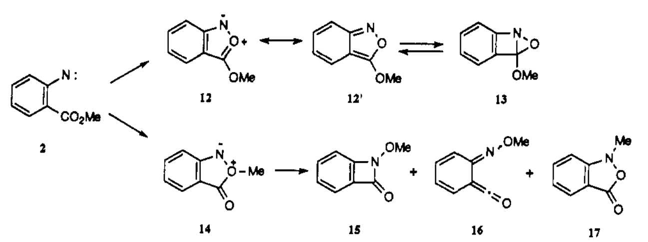
[12] (a) Chapman, O. L.; Sheridan, R. S.; LeRoux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 6245. (b) Chapman, O. L.; Sheridan, R. S.; LeRoux, J. P. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 334.

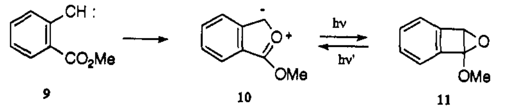
[13] (a) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683. (b) Chapman, O. L.; Johnson, J. W.; McMahon, R. J.; West, P. R. *Ibid.* **1988**, *110*, 501.

[14] Murata, S.; Ohtawa, Y.; Tomioka, H.; *Chem. Lett.* **1989**, 853. See also: Tomioka, H.; Kobayashi, N.; Murata, S.; Ohtawa, Y. *J. Am. Chem. Soc.* **1991**, *113*, 8771.

Scheme II



(methoxycarbonyl)phenyl)carbene (**9**), somewhat analogous to the present system, is trapped by the ortho substituent to generate the corresponding carbonyl ylide **10**, which is in photoequilibrium with the corresponding oxirane **11** (eq 6). The nitrenic center



(6)[14]

can, a priori, interact with the ester in two ways, that is, carbonyl oxygen and/or alkoxy oxygen. The interaction with the carbonyl oxygen will produce carbonyl ylide **12**, while that with the alkoxy oxygen will lead to oxonium ylide **14**. In analogy with the reactions observed for the carbene (**9**),[14] one can propose the products **13**–**17** starting from either of the ylides (Scheme II). An examination of the observed IR spectrum in terms of that expected for those proposed products suggests that carbonyl ylide **12** seems to not be a plausible precursor leading to the observed products, since neither 2,1-benzisoxazole **12′**, a canonical form of **12**, nor expoxide **13**, presumed to be produced by photochemical ring closure of **12′** is expected to show strong absorption bands in the carbonyl (1857 cm^{-1}) or ketene (2118, 2088 cm^{-1}) stretching regions. Moreover, it is not easy to draw a simple photochemical pathway starting from **12** to the products having ketene functional groups.

On the other hand, analysis of the reactions expected for oxonium ylide **14** suggests that this ylide seems to be a more promising candidate. Thus, intramolecular pathways for the ylides within matrices might be the Stevens rearrangement which can produce three products (**15**–**17**) according to the mode of the migration. Thus, acyl migration affords α-lactam **15**, while a methyl shift gives rise to oxazolone **17**. Oximino ketene **16** will also be formed either by electrocyclic reaction in **14** or by photochemical ring opening of lactam **15**. The product IR spectrum seems to match well with those expected for the proposed products. Thus, the ketene bands of **C** and **D** could be ascribable to those of **16**, which can exist as a mixture of geometrical isomers, while the C=O stretching absorption of **E** must be assignable to that of either **15** or **17**. Among those products, isoxazolone **17** which is a known compound and was prepared according to the reported[15] procedure exhibited its C=O absorption band at 1789 cm^{-1} in an Ar matrix at 10 K, which is completely different from that observed for **E**. On the other hand, the carbonyl stretching absorption bands for *N*-*tert*-butylazetinones are reported[16] to appear at 1812 cm^{-1}.

Thus, we wish to propose that the most probable structure for **E** is **15**, while products **C** and **D** must be a geometrical mixture of **16**. This assignment was further supported by the recent observation of Dunkin and his co-workers[17] that 1-methylbenzazetinone (**19**, ν(=O) 1843 cm^{-1}) generated and trapped in solid Ar by the thermolysis of 1-methyl-1,2,3-benzotriazin-4(1*H*)-one (**18**) undergoes ring opening upon irradiation with light of $\lambda < 380$ nm to imino ketene **20** (ν(C=C=O) 2125 cm^{-1}), which is reconverted to azetinone **19** upon irradiation with light of $\lambda >$ 400 nm (eq 7). The characteristic IR absorption bands of the products as well as the photointerconvertible nature of the reaction mixtures are very similar in both reaction systems.

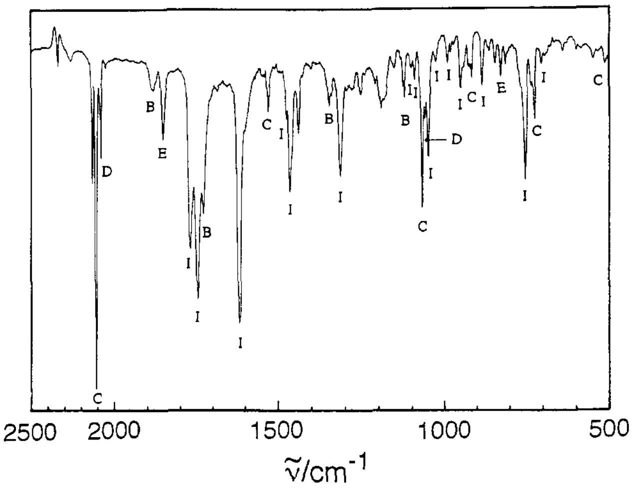
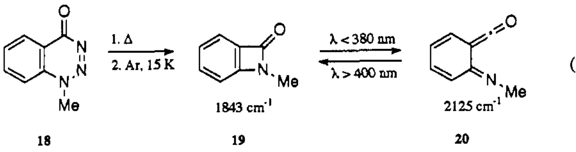
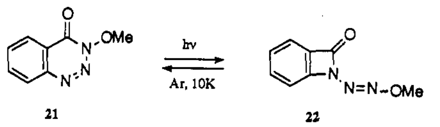


Figure 3. IR spectrum obtained after irradiation of *N*-methoxyisatin (**23**) in Ar at 10 K. Bands labeled I are **23**.



(7)[17]

In order to obtain unambiguous evidence to support the above assignment, we tried to generate those photoproducts from other possible precursors. Irradiation of matrix-isolated 3-methoxy-1,2,3-benzotriazin-4-one (**21**),[18] which is expected[19] to lose molecular nitrogen, however, did not result in elimination of nitrogen but produced 1-(methoxyazo)benzazetinone (**22**), which is in photoequilibrium with **21** (eq 8). On the other hand,



(8)[20]

irradiation ($\lambda > 350$ nm) of *N*-methoxyisatin (**23**) in an Ar matrix at 10 K resulted in a decrease in the starting material absorption bands and a concurrent growth of the absorption due to CO (2134 cm^{-1}) and other products' absorption bands (Figure 3). Detection of CO clearly indicates that **23** undergoes photodecarbonylation which should leave azetinone **15** and/or ketenes **16**. Careful comparison of those product bands in Figure 3 with that observed in the photolysis of **1** in Figure 1 immediately indicated that all the product bands ascribable to those of not only **C**, **D**, and **E** but also **B** completely coincided with each other (eq 9). Moreover, photointerconversion was also attained in this case. Thus, irradiation of the initial photomixture with light of $\lambda > 420$ nm resulted in growth of the bands at 1857 cm^{-1} (**E**), while irradiation with light of $\lambda > 300$ nm reproduced the bands at 1887 (**B**), 2118 (**C**), and 2088 cm^{-1} (**D**).

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[15] (a) Wierenga, W.; Evans, B. R.; Zurenko, G. E. *J. Med. Chem.* **1984**, *27*, 1212. (b) Wierenga, W.; Harison, A. W.; Evans, B. R.; Chidester, C. G. *J. Org. Chem.* **1984**, *49*, 438.

[16] (a) Olofson, R. A.; Vander Meer, R. K.; Stourans, S. *J. Am. Chem. Soc.* **1971**, *93*, 1543. (b) Olofson, R. A.; Vander Meer, R. K.; Hoskin, D. H.; Bernheim, M. Y.; Strourans, S.; Morrison, D. S. *J. Org. Chem.* **1984**, *49*, 3367.

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[19] (a) Burgess, E. M.; Milne, G. *Tetrahedron Lett.* **1966**, 93. (b) Ege, G. *Chem. Ber.* **1968**, *101*, 3079. (c) Ege, G.; Pasedach, F. *Ibid.* **1968**, *101*, 3089. (d) Hey, D. H.; Rees, C. W.; Todd, A. R. *J. Chem. Soc. C* **1968**, 1028. (e) Bashir, N.; Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1* **1973**, 868.

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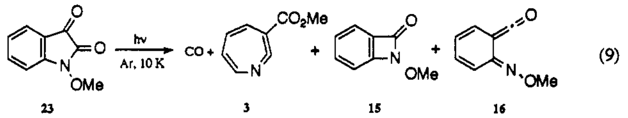


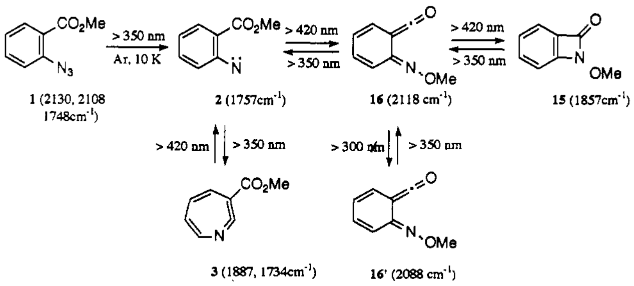
(9)

Product **A** was not assigned at this stage. Apparently, this product was not appreciably detected in the photolysis of isatin **23** but might be involved in the photointerconversion including **B**–**E**. Analysis of the IR spectrum obtained in the photolysis of **1** suggests that **A** is formed by irradiation of **1** with light of λ > 350 nm and decomposed not by the light of λ > 420 nm but by the light of λ > 300 nm, forming **B**, **C**, and **D**. The observations imply that **A** is a rather photosensitive intermediate involved in the photointerconversion. Only a slight shift of the C=O stretching absorption band in going from **1** to **A** and **A** to **B** again suggested that methoxycarbonyl groups were intact in these transformations. The most plausible candidate for **A** which is in accord with the presently available data is, then, (*o*-(methoxycarbonyl)phenyl)nitrene (**2**) itself. Sheridan and his co-workers[5g] have shown that irradiation of phenyl azide in 12 K Ar with light of 334 nm, which is not absorbed by phenylnitrene, results in the detection of triplet phenylnitrene as the major primary photoproduct along with a small amount of didehydroazepine, which, in turn, is formed as the major product under the broad-band irradiation conditions. Presumably, triplet ((methoxycarbonyl)phenyl)nitrene **2** was formed upon photolysis of **1** with the λ > 350 nm light in competition with the formation of didehydroazepine **3**. Triplet nitrene **2** is then decomposed by the shorter wavelength (λ > 300 nm) irradiation but not upon irradiation with the longer wavelength (λ > 420 nm) light. No appreciable formation of **2** in the photolysis of **23** can be interpreted, then, as indicating that **2** must be photolabile to the light which decomposes **23** and therefore produces either **3** or **15** and **16** before it accumulates to such an extent that it can be visible in the IR spectrum. It has been suggested[5g] that there may be a readily accessible excited state of phenylnitrene with a proclivity toward rearrangement.

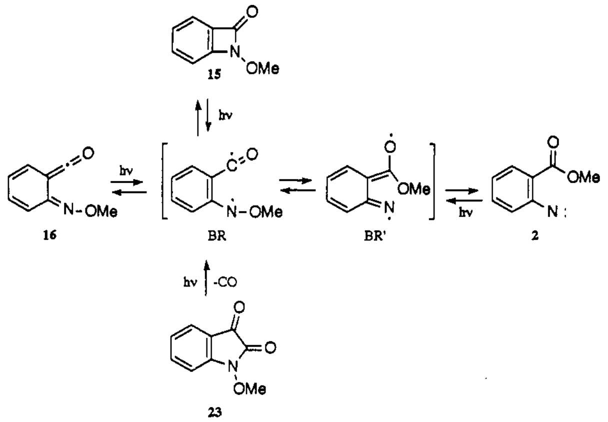
Based upon the above assignment, we wish to propose the overall reactions for the photolysis of **1** on Ar matrix as outlined in Scheme III. Thus, irradiation (λ > 350 nm) of **1** generates (1-(methoxycarbonyl)phenyl)nitrene (**2** = **A**), which either undergoes ring expansion to produce didehydroazepine **3** (= **B**) or gives rise to imino ketene **16** (= **C**). The imino ketene then undergoes either photocylization forming azetinone **15** (= **E**), upon irradiation with light of λ >420 nm, or geometrical isomerization leading to the isomer **16′** (= **D**).

There are several comments concerning the mechanism for the interconversion. First, what is the mechanism of the interconversion between **2** and **16**? One may propose that the nitrenic center interacts with the methoxycarbonyl oxygen forming oxonium ylide (i.e., **14**) which then undergoes Stevens rearrangement, as is shown in Scheme II. However, there are several observations which can not be explained by this mechanism. First, the ylidic intermediate **14** would undergo methyl migration producing **17** in competition with acyl migration leading to **15**. However, no trace of bands due to oxazolone **17** was detected in the photomixture, although the radical-pair mechanism proposed[21] for the Stevens rearrangement may explain the absence of this product (**17**). Second, we are not able to detect absorptions ascribable to the putative oxonium ylide intermediate **14**. Formation of such an ionic intermediate in noble gas matrices where solvation is not attained might be highly unfavorable. Finally, the mechanism is not applied to explain the backward reaction, that is, photochemical regeneration of **2** from **16**. The simplest explanation for this reaction would be, then, a 1,4-N → C shift of the MeO group in the excited state of **16**. The exact electronic nature of the excited states is not clear, but, by analogy with those of the related compounds, e.g., *o*-quinodimethane,[22] they may be regarded as 1,4-biradical species (BR). An alternative pathway for the photointerconversion of **2** to **16** may be, then, a 1,4-C → N MeO shift in the excited-state nitrene **2** generating common 1,4-biradical followed by the electron redistribution. The scheme can equally reasonably explain not only the formation of the same products by the photodecarbonylation of isatin **23** as well as by the photo ring cleavage of azetinone **15**, both of which can generate the BR, but also the completely reversible nature of the present reaction (Scheme IV).

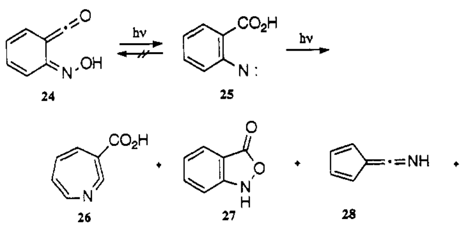
Scheme III



Scheme IV



It is very interesting to comment on the chemistry of phenylnitrenes having similar functional groups at the ortho position upon irradiation within matrices in this connection. (2-Carboxyphenyl)nitrene (**25**), for instance, either undergoes ring expansion to produce azacycloheptatetraene **26** or forms a mixture of 2,1-benzisoxazol-3(1*H*)-one (**27**) and carbonylcyclopentadiene imine **28** irreversibly (eq 10).[23] The latter two products are



(10)[23]

explained in terms of intramolecular O–H insertion of the nitrene and intramolecular hydrogen abstraction followed by decarboxylation and rearrangement, respectively. This implies that the hydroxy group is so reactive that it is trapped by the nitrenic center before it undergoes migration to form carbonyl oximino benzene **24**, although **24** can generate the nitrene upon irradiation, presumably via 1,4-OH migration. (2-Carbamoylphenyl)nitrene

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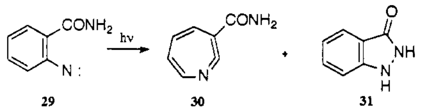
[21] Johnson, A. *W. Ylide Chemistry*; Academic Press: New York, 1966.

[22] (a) Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 361. (b) Netto-Frreira, J. C.; Scaiano, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 5800.

[23] Tomioka, H.; Ichikawa, N.; Komatsu, K. *J. Am. Chem. Soc.* **1992**, *114*, 8045.

[24] Tomioka, H.; Nakayama, T., unpublished observation.

(**29**) is also trapped by the amido NH bond to form **31** in competition with ring expansion forming **30** (eq 11).[24] On the



29 30 31 (11)[24]

other hand, phenylnitrenes bearing an acetyl or formyl group at the ortho position also undergo irreversible interaction with the ortho substituent, no migration leading to ketene being observed.[24]

Thus, the completely interconvertible photochemical transformation involving structurally different intermediates, i.e., **3**, **2**, **16**, and **15**, observed here is not only unprecedented but also not readily applicable to the related systems. It is also especially intriguing to note here that the phenylnitrene–pyridylmethylene photointerconversion usually occuring on the very slippery energy surface with many different entry points is channeled into a new and equally slippery energy surface once a methoxycarbonyl group is introduced at the ortho position of the phenylnitrene and that this new energy surface also has different entry points where even the isatin is found to be a precursor for the phenylnitrene involved in this new photointerconversion.

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 or JNM-EX 270 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). HPLC and GPC were undertaken with a JASCO 800 chromatography equipped with a UVIDEC-100-II UV/VIS detector using a Fine pack C18-T5 column (4.6 × 25 cm) and Shodex GPC H2001 (20 mm × 50 cm) column, respectively.

Matrix-Isolation Spectroscopy. Matrix experiments were performed by standard techniques[23,25] using an Iwatani Cryo Mini closed-cycle helium cryostat. For IR experiments, a CsI window was attached to the copper holder at the bottom of the cold head. Two opposing parts 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 a quartz outer window were used. The temperature of the matrix was controlled by an Iwatani TCU-1 controller (gold vs chromel thermocouple).

Argon (Seitetsu Chemicals, 99.999%) 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.

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

Materials. 2-(Methoxycarbonyl)phenyl Azide (1).[26] To a stirred solution of 2-azidobenzoic acid[27] (1.22 g, 7.48 mmol) in benzene (10 mL) was added thionyl chloride (5 mL) and the resulting mixture was refluxed for 4 h. After excess thionyl chloride was evaporated as an azeotropic mixture with benzene, the residue was dissolved in anhydrous pyridine (5.2 mL) and cooled on an ice bath. Methanol (5 mL) was added to the cooled and stirred solution, and the mixture was poured onto a 2 mM HCl solution followed by extraction with Et_2O. The organic layer was washed with a 5% KOH aqueous solution and water and dried over $MgSO_4$. Evaporation of the solvent produced **1** as a yellowish oil, which was purified by preparative TLC immediately before irradiation: ^{1}H NMR (CCl_4) δ 3.78 (s, 3H), 6.94–7.08 (m, 2H), 7.20–7.42 (m, 1H), 7.68 (d, J = 8.0 Hz, 1H); IR (Ar, 10 K) 2130 s, 2108 s, 1748 m, 1732 s, 1630 m, 1485 m, 1433 m, 1307 s, 1257 s, 1253 s, 1193 m, 1127 m, 1083 m, 754 s cm^{-1}.

Methyl Diazo-3-pyridylacetate (6). To a stirred solution of methyl 3-pyridylacetate[28] (166 mg, 1.10 mmol) and KF–Al_2O_3[29] (250 mg) in anhydrous acetonitrile (7 mL) was added tosyl azide (197 mg, 1.00 mmol) in acetonitrile (1 mL) at room temperature, and the mixture was stirred for 3 days. After filtration of KF–Al_2O_3 and evaporation of the solvent, the residue was extracted with Et_2O. Evaporation of the ether in vacuo gave **6** as an orange solid: 50.8%; mp 45–48 °C; ^{1}H NMR (CCl_4) δ 3.86 (s, 3H), 7.23 (dd, J = 6.0, 6.3 Hz, 1H), 7.72–7.90 (m, 1H), 8.26–8.40 (m, 1H), 8.61 (d, J = 3.0 Hz, 1H).

3-(Methoxycarbonyl)-*v*-triazolo[3,4-*a*]pyridine (8).[30] This was prepared according to the modified procedure of Regitz.[5] Thus, to a stirred solution of methyl 2-pyridylacetate[31] (200 mg, 1.33 mmol) and KF–Al_2O_3 (500 mg) in anhydrous acetonitrile (15 mL) was added tosyl azide (158 mg, 0.80 mmol) in acetonitrile (2 mL) at room temperature, and the mixture was stirred overnight. To the residue obtained after filteration of KF–Al_2O_3 and evaporation of solvent was added cooled water (1 mL) to produce a brownish solid, which was filtered and dried in vacuo: 19.1%; mp 138–141 °C; ^{1}H NMR (CCl_3) δ 4.04 (s, 3H), 7.14 (dd, J = 8.2, 8.0 Hz, 1H), 7.54 (dd, J = 8.2, 8.1 Hz, 1H), 8.42 (d, J = 8.1 Hz, 1H), 8.80 (d, J = 8.0 Hz, 1H).

1-Methyl-2,1-benzisoxazol-3(1*H*)-one (17).[15a] To a stirred solution of *N*-(hydroxymethyl)-2,1-benzoisoxazol-3(1*H*)-one[15b] (46 mg, 0.28 mmol) and Ag_2O (0.13 g, 0.57 mmol) in *N*,*N*-dimethylformamide (1 mL) was added methyl iodide (0.05 mL, 0.84 mmol), and the mixture was stirred overnight at room temperature. The mixture was filtered and diluted with EtOAc (20 mL). The organic layer was washed with water, 5% aqueous Na_2CO_3, and brine, dried (Na_2SO_4), and concentrated. The residue was separated by preparative TLC with 30% EtOAc/*n*-hexane to give **17** as a yellow oil: 62%; ^{1}H NMR (CCl_3) δ 3.38 (s, 3H), 7.07–7.34 (m, 2H), 7.55–7.87 (m, 2H); MS *m/e* (rel intensity) 149 (M$^+$, 100), 104 (42), 77 (33); IR (Ar, 10 K) 1789 s, 1621 s, 1482 w, 1459 w, 1334 w, 1125 m, 1020 w, 1011 w, 759 w, 680 w cm^{-1}.

***N*-Methoxyisatin (23).** To a stirred solution of 2-nitrobenzoyl chloride, prepared from 300 mg (1.8 mmol) of 2-nitrobenzoic acid and thionyl chloride, in anhydrous Et_2O (5 mL) was added a diazomethane solution, prepared from 2.14 g (10 mmol) of *N*-methyl-*N*-nitro-*p*-toluenesulfonamide in (5 mL), all at once. After being undisturbed for 1 h at room temperature, the mixture was carefully condensed to ca. $^1/_8$ of the original volume and the precipitated (2-nitrobenzoyl)diazomethane was filtered and washed with the ether. The diazomethane was added to the mixture of acetic acid (1.5 mL) and formic acid (3 drops), and the mixture was heated to reflux for 5 min and allowed to stand overnight. Filteration of the solid followed by washing with Et_2O gave crude *N*-hydroxyisatin[32] as a dark red solid: 9.7%; mp 186 °C dec.

The crude hydroxyisatin (16 mg, 0.098 mmol) was dissolved in $NaHCO_3$ (20 mg) in water (1 mL). To the resulting purple solution was added Me_2SO_4 (11 mL, 0.12 mmol), and the mixture was stirred at room temperature until the purple color disappeared. The mixture was extracted with Et_2O, and the organic layer was dried (Na_2SO_4) and evaporated. The crude product was purified by gel-permeation chromatography with $CHCl_3$ to produce **23** as orange crystals: 81%; mp 110–113 °C dec; ^{1}H NMR (CCl_3) 4.06 (s, 3H), 6.96–7.24 (m, 2H), 7.48–7.68 (m, 2H); MS *m/e* (rel intensity) 177 (M$^+$, 34), 149 (68), 146 (57), 119 (10), 104 (23), 92 (15), 91 (100), 90 (72), 78 (69), 76 (19), 64 (32), 63 (34); IR (Ar, 10 K), 1773 vs, 1750 vs, 1620 vs, 1464 s, 1314 s, 1049 m, 881 m, 752 s cm^{-1}.

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