group.[10] No EPR signal (spectra taken at room temperature and at 77 K) could be obtained from the powder nor from the ethanol solution, indicating that no unpaired electron is present in this compound, which excludes the presence of a superoxo species. This leaves two possible structural formulas for this compound viz. $[\mathrm{Co}^{(II)}\mathrm{Co}^{(III)}(\mathrm{bidhx})_2(\mathrm{H_2O})(\mathrm{O_2}^{2-})]^{3+}$ or $[(\mathrm{Co}^{(III)})_2(\mathrm{bidhx})_2(\mathrm{OH}^-)(\mathrm{O_2}^{2-})]^{3+}$ of which the latter seems the most likely.

The structure appeared to be incommensurate,[11] which was concluded from the high thermal anisotropy along the *b*-axis of all atoms. The structure was therefore refined with a reduced reflection set. The reflections with $(\sin \Theta/\lambda) < 0.30$ were omitted, which resulted in lower $R_f$ and $R_w$ values, and better standard deviations.

An ORTEP projection of the dimeric cation is shown in Figure 1. A twofold axis runs through the hydroxo group and the middle of the dioxygen molecule. For clarity the (disordered) nitrate anions have been omitted.

In $[\mathrm{Co_2(bidhx)_2(O_2)(OH)}](\mathrm{NO_3})_3$ the ligand coordinates tetradentate, with the two imidazole nitrogens in axial positions. The two thioether sulfurs are cis coordinated with relatively short Co-S distances compared with other crystal structures with this and a similar ligand.[12,13] The two cobalt ions are bridged by a hydroxo group and a peroxo group thus completing the octahedral coordination sphere of the cobalt(III) ions.

The cobalt-dioxygen bond distance is 1.877 (6) Å, and the cobalt-hydroxo bond distance is 1.924 (5) Å, which is quite normal for this kind of compounds.[1] The distance between this hydroxy ion and one of the nitrate oxygens is 2.90 (2) Å, indicating the presence of a hydrogen bridge. Therefore, the O atom must be part of a hydroxy or a water molecule. The cobalt-sulfur coordination distances are 2.245 (2) and 2.302 (2) Å. These Co-S distances are rather short. Coordination compounds of divalent metals with the same ligand have metal-sulfur distances in the range of 2.5-2.8 Å.[9] However, other cobalt(III)-thioether complexes are known, in which the cobalt to sulfur distances are about 2.27 Å.[14] The cobalt-imidazole nitrogen distances are 1.919 (6) and 1.927 (5) Å, again rather short compared to other cobalt(III) imidazole compounds, where the distances vary from 1.95 to 2.05 Å.[15,16] The shorter distances, observed in the compound described here, are probably due to the chelating nature of the ligand.

The O-O bond distance is 1.38 (1) Å, which is quite short for a peroxo group when compared with the known structures of analogous compounds.[1] The average O-O bond distance reported for peroxo groups is about 1.46 Å, while the average O-O bond distance reported for bridging superoxo groups is 1.34 Å. The cobalt-dioxygen bond angle, however, is 110.9 (3)°, which is normal for peroxo coordination. The Co-O-O-Co torsion angle is 60.2°, which is also quite normal for doubly bridged dicobalt peroxo complexes.[17]

The study of the catalytic properties and other spectroscopic properties of this compound are in progress.

**Acknowledgment.** We are indebted to Prof. Dr. J. Reedijk for his stimulating interest in this study and to Dr. R. A. G. de Graaff for his assistance in the determination of the crystal structure.

**Supplementary Material Available:** Tables of atomic coordinates, thermal parameters, and a full listing of bond lengths and bond angles (6 pages); tables of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

---

(10) Bagger, S.; Gibson, K. *Acta Chem. Scand.* **1972**, *26*, 3788.

(11) Wolff, P. M. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallog.* **1977**, *A33*, 777.

(12) Bouwmann, E., de Gelder, R.; de Graaff, R. A. G.; Driessen, W. L.; Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 163.

(13) Van Rijn, J.; Driessen, W. L.; Reedijk, J.; Lehn, J.-M. *Inorg. Chem.* **1984**, *23*, 3584.

(14) Roecker, L.; Dickman, M. H.; Nosco, D. L.; Doedens, R. J.; Deutsch, E. *Inorg. Chem.* **1983**, *22*, 2022.

(15) Zimmer-Gasser, B.; Dash, K. C. *Inorg. Chim. Acta* **1981**, *55*, 43.

(16) Bigotto, A.; Zangrando, E.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 96.

(17) Lever, A. B. P.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 348.

---

# Benz[*cd*]indazole: Infrared Spectroscopic Study

Akira Yabe,* Koichi Honda, and Hiroshi Nakanishi

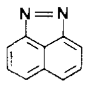
*National Chemical Laboratory for Industry*
*Tsukuba, 305 Ibaraki, Japan*

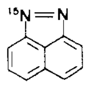
Richard A. Hayes and Orville L. Chapman

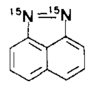
*Department of Chemistry, University of California*
*Los Angeles, California 90024*

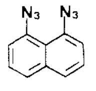
*Received February 22, 1988*

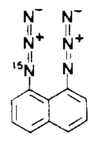
Benz[*cd*]indazole (**1**) is of interest as a simple heterocyclic system, and has been the subject of many unsuccessful synthetic attempts[1] before we (NCL group) succeeded in producing it by low-temperature photolysis of 1,8-diazidonaphthalene (**2**).[2] In our preliminary works, the first preparation of **1** has been characterized by UV-spectroscopy in an organic glassy matrix at 77 K from the photolysis of **2** and also by $^1$H, $^{13}$C, and $^{15}$N NMR spectroscopies.[3,4] However, its detailed structural feature has still been ambiguous because it could not be isolated in the solid state at room temperature and was relatively stable only in dilute solution. We now report further structural information about **1** on the basis of the IR spectroscopic experiments in an argon matrix at cryogenic temperature.

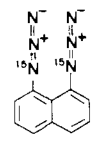

1


1a


1b


2


2a


2b

For the IR spectroscopic study, two kinds of $^{15}$N-labeled 1,8-diazidonaphthalenes (**2a** and **2b**), in addition to the unlabeled compound **1**, were prepared as precursors of **1a** and **1b**.[5] A mixture of 1,8-diazidonaphthalene (**2**, **2a**, or **2b**) and argon (1:200 to 1:500) was deposited on the CsI crystal plate at 20 K by the matrix isolation technique with a closed-cycle refrigerator system (Air Products CS 202). Photochemical changes upon the irradiation of **2**, **2a**, and **2b** with >300-nm light (through a UV-cut filter with a 500 W super-high-pressure mercury lamp) were followed by IR spectroscopy.

With the increase of irradiation time, the decrease of azido groups ($\mathrm{N_3}$: 2100-2150 cm$^{-1}$) from the starting azide **2**[6] and the appearance of new peaks at 1450, 1285, 1232, 1220, 1210, 1198, 1168, 1150, 1025, 990, 978, 904, 814, 764, and 608 cm$^{-1}$ were observed (Figure 1a). These new peaks should be ascribed to **1**, because the corresponding UV spectrum of the sample prepared under the same conditions, as shown in Figure 2, was almost

---

(1) (a) Bradbury, S.; Rees, C. W.; Storr, R. C. *Chem. Commun.* **1969**, *1429*. (b) Alder, R. W.; Niazi, G. A.; Whiting, M. C. *J. Chem. Soc. C* **1970**, 1693. (c) Bradbury, S.; Rees, C. W.; Storr, R. S. *J. Chem. Soc., Perkin Trans. 1* **1972**, 68.

(2) Yabe, A.; Honda, K.; Oikawa, S.; Tsuda, M. *Chem. Lett.* 1976, 823.

(3) Nakanishi, H.; Yabe, A.; Honda, K. *J. Chem. Soc., Chem. Commun.* **1982**, 86.

(4) Yabe, A.; Honda, K.; Nakanishi, H.; Someno, K. *Chem. Lett.* **1984**, 1407.

(5) Compounds **2a** and **2b** were prepared via 1,8-di[($^{15}$N,N)- or ($^{15}$N,$^{15}$N)]nitronaphthalene obtained by nitration of 1-nitronaphthalene or naphthalene with $^{15}$N-labeled nitric acid (90 atom% $^{15}$N; 8.34 M), respectively. The introduction of $^{15}$N to the naphthalene ring has been established: Zollinger, H. *Azo and Diazo Chemistry*; Interscience: New York, 1961; p 147.

(6) The complete spectrum of **1** in an argon matrix at 20 K: 3076, 2272 (s), 2257 (s), 2197 (s), 2137 (s), 2122 (s), 2107 (s), 2092 (m), 2069 (m), 2054 (m), 1628 (m), 1601 (m), 1586 (m), 1579 (m), 1515, 1466, 1440, 1429, 1414, 1391 (s), 1376, 1361, 1342, 1327, 1316 (s), 1306, 1297 (s), 1170, 1155, 1102, 1023, 963, 817 (m), 794, 757 (m), and 689 (m) cm$^{-1}$.

0002-7863/88/1510-4441$01.50/0

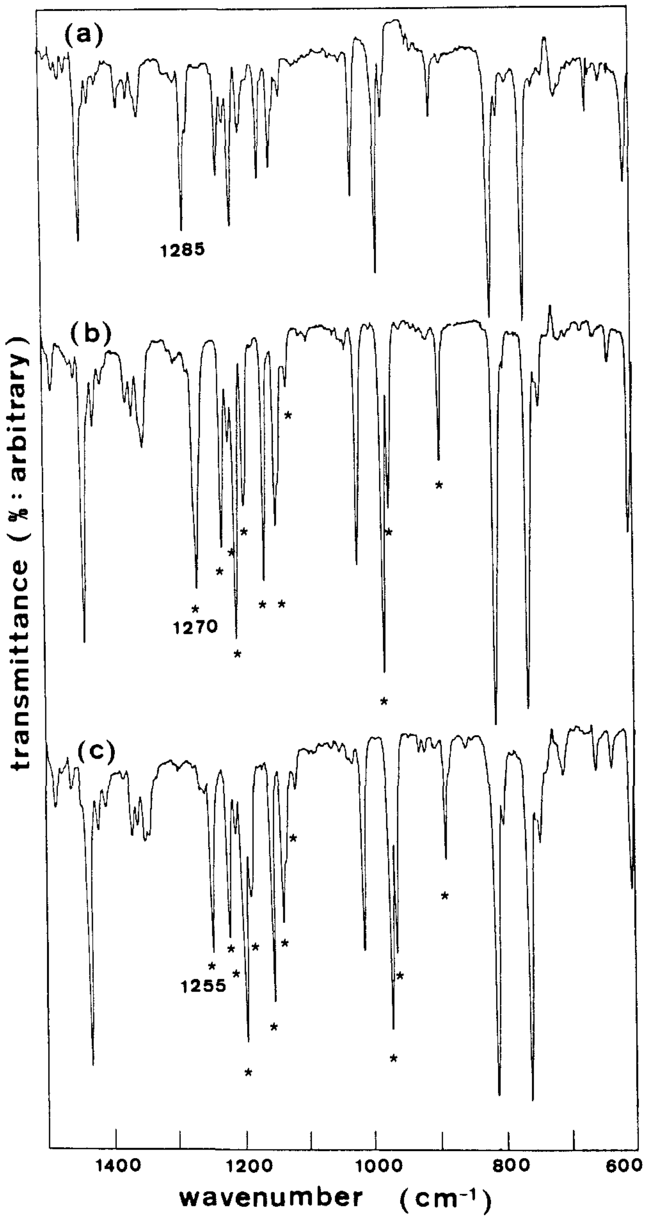


**Figure 1.** Infrared spectra after the photolysis of **2**, **2a**, and **2b** in an argon matrix at 20 K upon the irradiation with a > 300-nm light: these spectra are ascribed to **1** for (a), **1a** for (b), and **1b** for (c). The bands marked with an asterisk are shifted to lower frequencies compared with those of (a).

identical with those that we had already identified in organic glassy matrices at 77 K.[2]

By comparing the IR spectra of $^{15}$N-labeled benz[*cd*]indazoles (**1a** and **1b**) with that of **1**, isotopic shifts were observed for several bands in the 900–1285 cm$^{-1}$-region (Figure 1). IR spectra of $\mathrm{N{=}N}$ bonds conjugated with aromatic rings have been studied in detail on the $^{15}$N-labeled *trans*- and *cis*-azobenzenes by Kübler and Lüttke.[7] They have reported that the $\mathrm{N{=}N}$ stretching vibration for *cis*-azobenzene is found at 1511 cm$^{-1}$, the corresponding band for the $^{14}\mathrm{N{=}}^{15}\mathrm{N}$ bond appears at 1486 cm$^{-1}$ with an isotopic shift, $\Delta\nu$ = 25 cm$^{-1}$, and the phenyl-N vibrations are at 1259, 1067, 920, and 866 cm$^{-1}$ with smaller isotopic shifts ($\Delta\nu$ = 1–6 cm$^{-1}$). On the basis of the isotopic effects of *cis*-azobenzene bands, we have assigned tentatively the isotope related bands of **1**, considering the much more strained structure of **1**. Among the bands with isotopic shifts, the highest frequency (1285 cm$^{-1}$) having the largest shift should be assigned to the $\mathrm{N{=}N}$ stretching. Other peaks with smaller isotopic shifts may be assigned to the naphthylene-N,N vibrations. The observed isotopic shifts for the $\mathrm{N{=}N}$ stretching vibration (1285 cm$^{-1}$) are 15 cm$^{-1}$ for **2a** (1270 cm$^{-1}$) and 30 cm$^{-1}$ for **2b** (1255 cm$^{-1}$). On the other hand, the possible maximum $^{15}$N isotopic shifts calculated from the simple equation of diatomic harmonic oscillator are 22 cm$^{-1}$ for **2a** and 44 cm$^{-1}$ for **2b**. The discrepancy between the observed and calculated values is 32% smaller in both **2a** and **2b**, suggesting that the 1285 cm$^{-1}$ normal coordinate is due 2/3 to the N–N stretch and 1/3 to motions of other atoms.

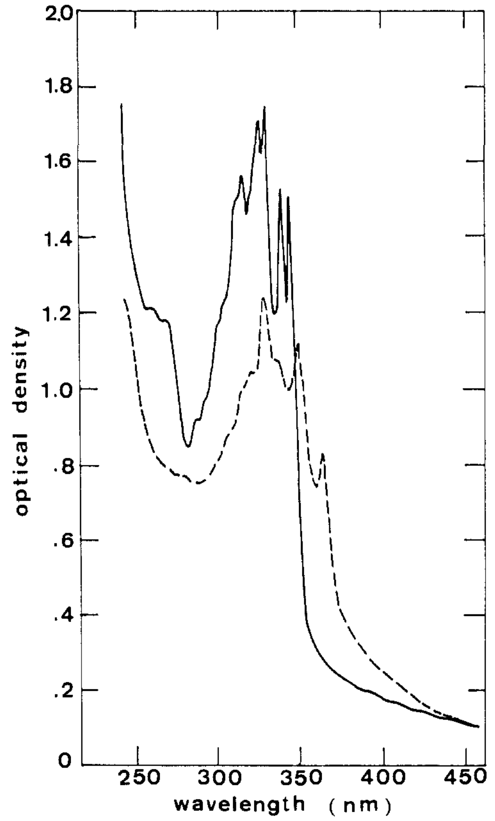
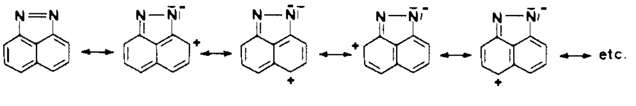
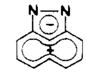


**Figure 2.** UV–vis absorption spectra for the photolysis of **1** before irradiation (solid curve) and after irradiation (dashed curve) in an argon matrix at 20 K.

Moreover, the 1285-cm$^{-1}$ band, which was assigned tentatively to the $\mathrm{N{=}N}$ stretching, is remarkably low as compared with the $\mathrm{N{=}N}$ stretching bands of usual azo compounds studied so far. Most azo-group frequencies have been reported to be 1600–1400 cm$^{-1}$, and these would tend toward lower frequencies with delocalization of $\mathrm{N{=}N}$ double bonds.[8] In the case of **1**, the polar resonance structures as shown below are possible because of an aza analogue of the nonalternate hydrocarbon, acenaphthylene. Therefore, the five-membered ring involving two nitrogen atoms in **1** has a high electron density compared with the naphthalene ring. Consequently, **1** is represented by the formula **1c**, indicating the lack of double bond character for the $\mathrm{N{=}N}$ bond and the relief of steric strain at the peri position in the naphthalene ring. Thus, the observed spectral properties described above will suggest the structure **1c**.





1c

The structure assignment of **1** is further supported by some chemical reactivities and the spectral data reported in the previous

---

[7] Kübler, R.; Lüttke, W.; Weckherlin, S. *Z. Elektrochem.* **1960**, *64*, 650.

[8] Dolphin, D.; Wick, A. *Tabulation of Infrared Spectral Data*; John Wiley: New York, 1977; pp 425–427.

papers.[2,3] Differing from such stable aromatic azo compounds as benzo[*c*]cinnoline and indazole, **1** is too labile to isolate in the solid state at room temperature and turn into the deep blue-purple compound which is presumed to be the product from polymerization or self-condensation of **1**.[1,9] Addition of protic solvents, e.g., methanol, into the dilute solution of **1** gives the adduct of **1** with the protic solvents which was not definitely identified because of its lability.[10]

In conclusion, unusual properties of **1** as compared with typical aromatic azo compounds would be explained in the terms of the lack of usual double bond character for the N=N bond, which was elucidated by the IR spectroscopic studies.

---

[9] Deep blue-purple solids having $\lambda_{max}$ ca. 550 nm in the absorption spectrum. It was not characterized because it gave a wide streak on thin-layer chromatography and showed complicated peaks on $^1H$ and $^{13}C$ NMR spectra.

[10] In dilute solutions (e.g., ether:2-methylbutane:ethanol = 5:5:2) at room temperature it has characteristic absorption maxima at 331, 317, and 304 nm.

---

# Dimethoxycarbene: Direct Observation of an Archetypal Nucleophilic Carbene[†]

Robert A. Moss,* Marek Włostowski,[1] Shilan Shen, Karsten Krogh-Jespersen,* and Alexander Matro

*Department of Chemistry*
*Rutgers, The State University of New Jersey*
*New Brunswick, New Jersey 08903*

*Received March 7, 1988*

Difluorocarbene and methoxychlorocarbene are representative electrophilic and ambiphilic carbenes[2] that have been extensively studied and directly observed.[3,4] Dimethoxycarbene (DMC), perhaps the archetypal nucleophilic carbene,[2] is most frequently generated by pyrolyses of 7,7-dimethoxynorbornadiene derivatives.[5] Although much has been learned about its chemistry, these generative conditions are not easily adapted to *direct observation* of DMC.

We are therefore pleased to report the preparation of 3,3-dimethoxydiazirine (**1**), the facile generation of DMC,[6] the matrix isolation and ambient temperature UV spectra of DMC, and initial absolute kinetic studies of the carbene's reactions with methanol and alkenes. There have been many direct studies of triplet arylcarbenes[7] and singlet arylhalocarbenes[8,9] in solution, but this is the first observational study of a nucleophilic carbene.

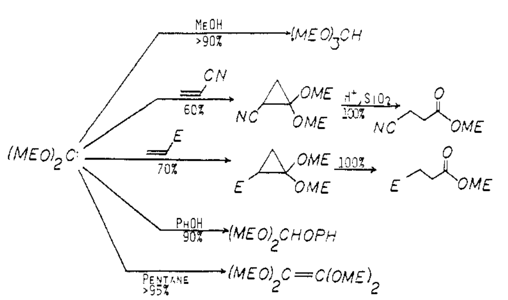


**Figure 1.** Reactions of DMC generated thermally from diazirine **1** at 25 °C; ME = methyl, PH = phenyl, E = COOMe. See text for discussion.

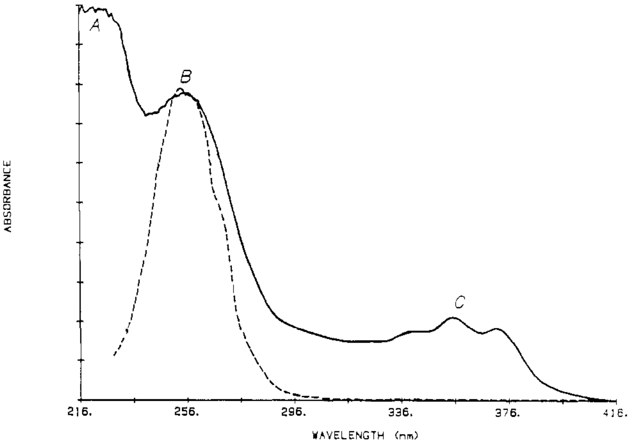
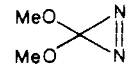


**Figure 2.** UV spectra of DMC in a 3-methylpentane glass at 77 K (solid line) and in pentane solution at 25 °C (dashed line). See text for assignments and discussion.



**1**

$(MeO)_2C{=}C(OMe)_2$

**2**

3-Chloro-3-methoxydiazirine[10] was converted to **1** by exchange[6b,9,11] with excess NaOMe in DMF at −30 to −50 °C for 30 min. Rapid extraction with cold pentane of a crushed ice/water quench of the reaction mixture, drying ($CaCl_2$, −20 °C, 20 min), and filtration through silica gave ~60% of diazirine **1** as a ~0.07 M pentane solution. Analogous solutions were used for all further experiments. The identification of **1** rests on its method of preparation,[6b,9] characteristic[10] UV spectrum ($\lambda_{max}$ 338 sh, 358, 372 nm), and decomposition products (see below).

Thermal decomposition of **1** in pentane was monitored at 372 nm over eight temperatures between 15 and 50 °C. The kinetics were first order, with $k = 5.43 \times 10^{-4}\ s^{-1}$, $\tau_{1/2} \sim 21$ min at 25 °C,[12] and $E_a = 18.9$ kcal/mol. The sole product was carbene dimer **2**,[13] identical in GC retention time and NMR spectrum to an authentic sample.[5e]

---

[†] Dedicated to Professor Gerhard L. Closs on the occasion of his 60th birthday.

[1] Visiting Scientist on leave from the Politechnika, Warsaw, Poland.

[2] Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58.

[3] $CF_2$: (a) Mitsch, R. A. *J. Am. Chem. Soc.* **1965**, *87*, 758. (b) Mitsch, R. A.; Rodgers, A. S. *Int. J. Chem. Kinet.* **1969**, *1*, 439. (c) Moss, R. A.; Mallon, C. B. *J. Am. Chem. Soc.* **1975**, *97*, 344. (d) Carr, R. W., Jr.; Peterson, D. G.; Smith, F. K. *J. Phys. Chem.* **1986**, *90*, 607. (e) Chowdhury, P. K.; Rama Rao, K. V. S.; Mittal, J. P. *Ibid.* **1988**, *92*, 102. (f) Tyerman, W. J. R. *Trans. Faraday Soc.* **1969**, *65*, 1188. (g) Cavell, R. G.; Dobbie, R. C.; Tyerman, W. J. R. *Can. J. Chem.* **1967**, *45*, 2849.

[4] MeOCCl: (a) Moss, R. A.; Fedorynski, M.; Shieh, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 4736. (b) Smith, N. P.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. II* **1979**, 1298. (c) Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 99. (d) Sheridan, R. S.; Kesselmayer, M. A. *Ibid.* **1984**, *106*, 436.

[5] (a) Hoffmann, R. W. *Acc. Chem. Res.* **1985**, *18*, 248. (b) Hoffmann, R. W.; Reiffen, M. *Chem. Ber.* **1976**, *109*, 2565. (c) Hoffmann, R. W.; Lillienblum, W.; Dittrich, B. *Ibid.* **1974**, *107*, 3395. (d) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 529. (e) Lemal, D. M.; Gosselink, E. P.; McGregor, S. D. *J. Am. Chem. Soc.* **1966**, *88*, 582. (f) Lemal, D. M.; Lovald, R. A.; Harrington, R. W. *Tetrahedron Lett.* **1965**, 2779. (g) Hoffmann, R. W.; Hauser, H. *Tetrahedron* **1965**, *21*, 891.

[6] (a) We reported the analogous generation of methoxyphenoxycarbene,[6b] but we have been unable to obtain transient spectra of this species. (b) Moss, R. A.; Włostowski, M.; Terpinski, J.; Kmiecik-Ławrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 3811.

[7] Schuster, G. B. *Adv. Phys. Org. Chem.* **1986**, *22*, 311. Scaiano, J. C. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z., Ed.; CRC Press: Boca Raton, FL, in press.

[8] Moss, R. A.; Ławrynowicz, W.; Turro, N. J.; Gould, I. R.; Cha, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7028, and earlier papers cited there. See, also: Eisenthal, K. B.; Moss, R. A.; Turro, N. J. *Science* (*Washington, D. C.*) **1984**, *225*, 1439.

[9] MeOCPh: Moss, R. A.; Shen, S.; Hadel, L. M.; Kmiecik-Ławrynowicz, G.; Włostowska, J.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 4341.

[10] Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

[11] Włostowska, J.; Moss, R. A.; Guo, W.; Chang, M. J. *Chem. Commun.* **1982**, 432. Moss, R. A.; Terpinski, J.; Cox, D. P.; Denney, D. Z.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 2743.

[12] Diazirine **1** is less stable than 3-methoxy-3-phenoxydiazirine, which has $\tau_{1/2} \sim 64$ min under comparable conditions.[6b]

[13] If methanol or water is present, methyl orthoformate is also formed.

0002-7863/88/1510-4443$01.50/0 © 1988 American Chemical Society