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Dye-Sensitized Photooxygenation of 4,6-Di-*tert*-butyl-2-diazo-1,2-benzoquinone

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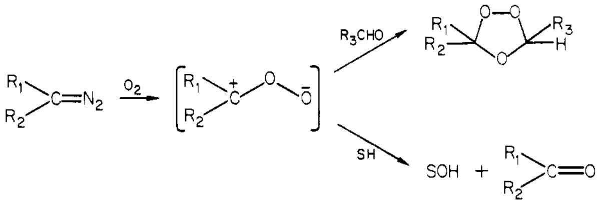
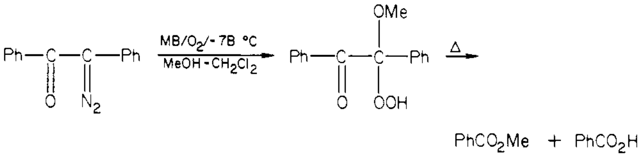
Oxygenation reactions of diazo compounds with molecular oxygen[1] have been intensively investigated in connection with the chemistry of carbonyl oxides. The latter are formed as intermediates in ozonation of alkenes and alkynes[2] and also could be models for intermediates in monooxygenase-catalyzed reactions.[3]

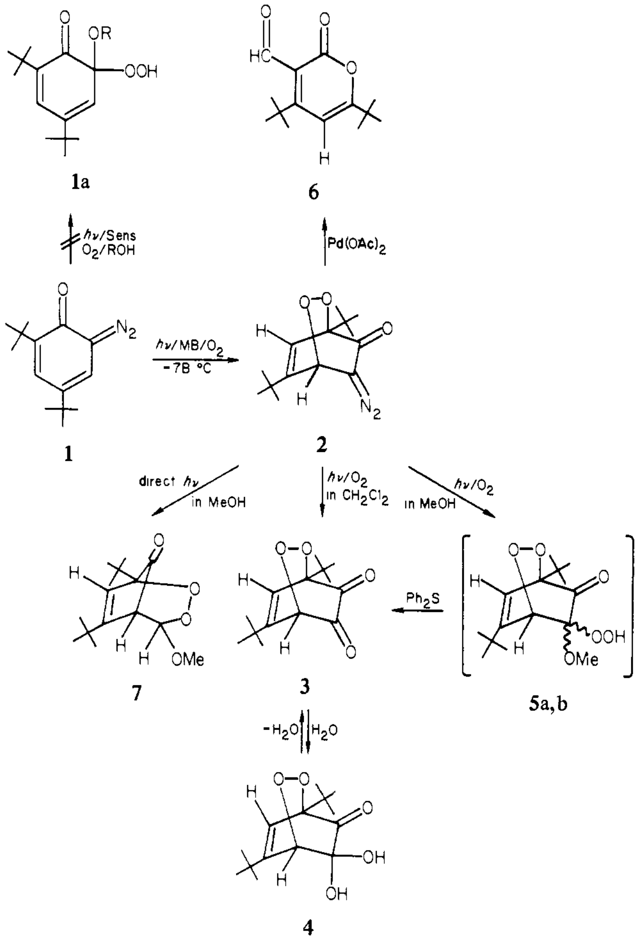


It is to be expected that carbonyl oxides derived from singlet oxygen oxygenation of diazo compounds would be trapped efficiently by nucleophiles, since they bear a similarity to the ozonation intermediates. In fact, we found that dye-sensitized photooxygenation of azibenzil in CH_2Cl_2–MeOH (1:1) at −78 °C produced the corresponding α-ketomethoxy hydroperoxide which spontaneously decomposed to methyl benzoate and benzoic acid upon warming to room temperature.[4]



As part of an investigation of biomimetic oxygenation reactions, we wished to photooxidize 4,6-di-*tert*-butyl-2-diazo-1,2-benzoquinone (**1**) in the hopes that we could produce the hydroperoxy hemiketal **1a**, a potential intermediate in pyrocatechase reactions.[5] However, dye-sensitized photooxygenation of **1** instead resulted in the formation of endoperoxide **2** in which the diazo group was unaffected (Scheme I).

Scheme I



Photooxygenation of **1** (0.1 M) at −78 °C in CH_2Cl_2 with methylene blue (10^{-4} M) sensitizer using a tungsten lamp filtered by Na_2CrO_4 (400 g/L)[6] gave **2**[7] and **3**[8] as major products with ratios which depended on irradiation times. Control experiments monitored by NMR spectroscopy showed that **2** was the sole initial oxidation product and was formed in 87% yield; **3** is a minor product at the point where **1** is completely consumed. Under the same conditions, **2** was slowly oxidized to **3** (76%) which was isolated as the stable hydrate **4**.[9] Compound **4** could be dehydrated to **3** at −28 °C without decomposition in the presence of molecular sieves. Photooxygenation of **1** in MeOH–CH_2Cl_2 (1:1) also led to **2** as the initial oxidation product; **2** subsequently reacted

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(1) (a) Kirmse, W.; Horner, L.; Hoffman, H. *Liebigs Ann. Chem.* **1966**, *31*, 419. (b) Bartlett, P. D.; Traylor, T. G. *J. Am. Chem. Soc.* **1962**, *84*, 3408. (c) Hamilton, G. A.; Giacin, J. R. *Ibid.* **1966**, *88*, 1584. (d) Murray, R. W.; Suzui, A. *Ibid*, **1971**, *93*, 4963. (e) Higley, D. P.; Murray, R. W. *Ibid.* **1974**, *96*, 3330. (f) Chaudlhary, S. K.; Hoyt, R. A.; Murray, R. W. *Tetrahedron Lett.* **1976**, 4235. (g) Hinrichs, T. A.; Ramachandran, V.; Murray, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 1282. (h) Sekiguchi, A.; Kabe, Y.; Ando, W. *Tetrahedron Lett.* **1979**, 233. (i) Ando, W.; Miyazaki, H.; Kohmoto, S. *Ibid.* **1979**, 1317. (j) Ando, W.; Kohmoto, S.; Nishizawa, K. *J. Chem. Soc., Chem. Commun.* **1978**, 894. (k) Daly, J. W.; Jerina, D. M.; Witkop, B. *Experientia* **1972**, *28*, 1129. (l) Ryang, H. S.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 2129.

(2) (a) For review: Belew, J. S., In "Oxidation"; Augustine, R. L., Ed.; Marcel Dekker: New York, 1969. (b) Criegee, R.; Wenner, G. *Ann.* **1949**, *564*, 9. (c) Criegee, R.; Lohaus, G. *Ibid.* **1953**, *533*, 6. (d) Criegee, R.; Kerchow, A.; Zink, H. *Chem. Ber.* **1955**, *88*, 1878. (e) Kwart, H.; Hoffman, D. M. *J. Org. Chem.* **1966**, *31*, 419. (f) DeMore, W. B.; Lin, C. L. *Ibid.* **1973**, *38*, 985. (g) Keary, R. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 6578.

(3) (a) Hamilton, G. A. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974; p 405. (b) Matsuura, T. *Tetrahedron* **1977**, *33*, 2869.

(4) The α-ketomethoxy hydroperoxide was isolated in ~80% purity (positive peroxide test with KI/HCl): ^1H NMR δ ($CDCl_3$ at 0 °C) 3.24 (3 H, s), 7.10–7.80 (8 H, m), 8.10 (2 H, d), 9.80 (1 H, br).

(5) (a) Nozaki, M. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974; p 135. (b) Vanneste, W. H.; Zuberbühler, A. *Ibid.*, p 371. (c) Matsuura, T.; Nishinaga, A.; Yoshimura, N.; Aria, T.; Omura, K.; Matsushima, H.; Kato, S.; Saito, I. *Tetrahedron Lett.* **1969**, 1673. (d) Nishinaga, A.; Itahara, T.; Matsuura, T. *Bull Chem. Soc. Jpn.* **1974**, *47*, 1811. (e) Tsuji, J.; Takayanagi, H.; *J. Am Chem. Soc.* **1974**, *96*, 7349. *Tetrahedron Lett.* **1976**, 1365. (f) Tsuji, J.; Takayanagi, H.; Sakai, I. *Ibid.* **1975**, 1245. (g) Sawaki, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 6292. (h) Sawaki, Y.; Foote, C. S., to be published. (i) Rogic, M. M.; Demmin, T. R.; Hammond, W. B. *J. Am. Chem. Soc.* **1976**, *98*, 7441. (j) Rogic, M. M.; Demmin, T. R. *Ibid.* **1978**, *100*, 5472. (k) Demmin, T. R.; Rogic, M. M. *J. Org. Chem.* **1980**, *45*, 1153, 2737, 4210. (l) Muto, S.; Bruice, T. C. *J. Am. Chem. Soc.* **1980**, *102*, 4472, 7559.

(6) The filter solution cuts off wavelengths shorter than 550 mm. With this filter, only methylene blue (MB) absorbs the incident light from a tungsten-halogen DWY lamp (650 W), which was operated at 70 V. Oxygen was bubbled through the solution during irradiation. Bleaching of MB was observed when the photooxygenation was carried out at room temperature.

(7) Compound **2**: mp 80 °C dec; ^1H NMR δ ($CDCl_3$ internal standard, 7.25 ppm) 1.14 (9 H, s), 1.18 (9 H, s), 5.63 (1 H, d, *J* = 2.2 Hz), 6.10 (1 H, d, *J* = 2.2 Hz); IR (Nujol) 2120, 1680 cm^{-1}; mass spectrum, *m/e* 236 (M − 28); ^{13}C NMR δ ($CDCl_3$ internal standard, 77.3 ppm) 27.4 (q), 34.6 (s), 35.0 (s), 60.1 (s), 73.7 (d), 89.6 (s), 118.6 (d), 160.7 (s), 189.9 (s); positive peroxide test with KI/HCl.

(8) Compound **3**: ^1H NMR δ ($CDCl_3$) 1.14 (9 H, s), 1.17 (9 H, s), 5.10 (1 H, d, *J* = 2.2 Hz), 6.47 (1 H, d, *J* = 2.2 Hz); ^{13}C NMR δ ($CDCl_3$) 27.3 (q), 27.4 (q), 34.8 (s), 35.4 (s), 82.0 (d), 90.3 (s), 123.9 (d), 158.1 (s), 181.5 (s), 184.5 (s), 184.1 (s); positive peroxide test with KI/HCl.

(9) Compound **4** (hydrate of **3**): mp 79 °C dec; ^1H NMR δ ($CDCl_3$) 1.15 (9 H, s), 1.16 (9 H, s), 3.72 (1 H, br), 3.78 (1 H, br), 4.83 (1 H, d, *J* = 2.3 Hz), 6.15 (1 H, d, *J* = 2.3 Hz); IR (Nujol) 3500, 1760 cm^{-1}; mass spectrum, *m/e* 209 (M − 61), 180; ^{13}C NMR δ ($CDCl_3$) 25.3 (q), 28.1 (q), 34.6 (s), 35.1 (s), 79.2 (d), 86.2 (s), 88.5 (s), 117.9 (d), 160.7 (s), 199.6 (s); positive peroxide test with KI/HCl. So far we have not determined which carbonyl is hydrated. Besides **3**, we observed the formation of a minor product (24%), which is less stable than **3** and sensitive to MeOH. The structure has not been determined yet.

0002-7863/81/1503-4951$01.25/0

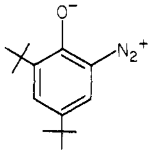
J. Am. Chem. Soc. 1981, 103, 4952-4954

quantitatively to give two isomers **5a,b**[10] (**5a**/**5b** = 6:4) of a methanol addition product. Upon warming, **5a,b** gave several decomposition products including **3** (30-64%). However, when Ph_2S was added to the solution immediately after irradiation at -78 °C and the solution subsequently warmed to room temperature, **3** was formed exclusively along with Ph_2SO,[11] indicating that oxygen-atom transfer occurred from **5a,b** to Ph_2S upon warming.[12] On the basis of this evidence, together with NMR data, it is reasonable to assume that the oxidation of **2** leads to a carbonyl oxide which reacts with MeOH to give both isomers of the α-ketomethoxy hydroperoxides **5a,b**.[4]

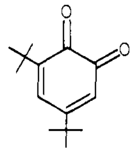
Thermolysis of **2** under N_2 in benzene afforded **6** (~40%)[13] along with some reversion to **1**. However, when the decomposition of **2** was catalyzed by $Pd(OAc)_2$ at room temperature, under N_2, **6** was obtained quantitatively. The formation of **6** is surprising, and must result from a deep-seated rearrangement, but the structure is secure.[13]

The photochemistry of **2** was also examined. Direct irradiation of **2** in MeOH at 0 °C using a tungsten lamp (no filter) resulted in the formation of the unusual rearranged peroxide **7** (95%).[14] Wolff rearrangement, which is a favorable process in most α-diazo ketones,[15] is not operative in this case.

The initial formation of **2** was unexpected since diazo groups are usually very susceptible to the attack of $^1O_2$.[1d-i] Stable endoperoxides have been shown to be derived from nonaromatic, polyaromatic, and vinyl aromatic systems,[16] but we expected the ketodiazodiene system to be sufficiently deactivated by the electron-withdrawing substituents to be unreactive. Photoreaction of 3,5-*tert*-butyl-*o*-benzoquinone **8** under similar conditions did not give any oxidation products. The results suggest an important role of the diazo group for the formation of **2**. The fact that there are considerable low-field shifts of the ring protons of **1** compared to those of **8** in the ^1H NMR[17] suggest a significant contribution of the resonance structure **1′**, which would be expected to deactivate the diazo group relative to the ring toward attack by $^1O_2$. The importance of structure **1′** has also been suggested in the thermal reactions of *o*-diazoquinones with ketenes and diazo compounds.[18] Futher investigation of the reaction as well as the chemistry of these peroxides is now in progress.



1′



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[10] After complete photooxygenation of **1** or **2** in CH_2Cl_2-MeOH (1:1) at -78 °C, the solvent was carefully removed at 0 °C. The residue was dissolved in $CDCl_3$ and transferred to an NMR tube. The spectrum was taken at different temperatures. ^1H NMR spectrum showed the formation of two products **5a,b** (ratio **5a**/**5b**=6:4). No other products were observed. ^1H NMR of **5a**: δ ($CDCl_3$, -50 °C) 1.06 (9 H, s), 1.09 (9 H, s), 3.36 (3 H, s), 4.84 (1 H, br), 4.98 (1 H, d, J = 2.0 Hz), 6.07 (1 H, d, J = 2.0 Hz). ^1H NMR of **5b**: δ 1.01 (9 H, s), 1.06 (9 H, s), 3.48 (3 H, s), 5.17 (1 H, d, J = 2.0 Hz), 6.10 (1 H, d, J = 2.0 Hz), 10.4 (1 H, br). The peaks at 4.8 and 10.4 ppm shifted to higher field with increasing temperature. Compound **5b** is less stable and decomposed more rapidly than **5a** upon warming to room temperature.

[11] Endoperoxides **2-4** did not oxidize Ph_2S under the conditions.

[12] For oxygen-atom transfer reactions by α-alkoxy hydroperoxides; see: (a) Rebek, J.; McCready, R.; Wolak, R. *J. Chem. Soc., Chem. Commun.* **1980**, 705. (b) Rebek, J. *Heterocycles* **1981**, *15*, 517.

[13] Compound **6**: mp 80 °C; ^1H NMR δ ($CDCl_3$), 1.30 (9 H, s), 1.36 (9 H, s), 6.30 (1 H, s), 10.30 (1 H, s); ^{13}C NMR δ ($CDCl_3$), 28.1 (q), 30.3 (q), 37.1 (s), 37.6 (s), 100.5 (d), 118.1 (s), 163.3 (s), 171.1 (s), 175.2 (s), 192.4 (d); IR (cm^{-1}) 2820, 2720, 1710, 1690, 1620; *mass spectrum*, *m/e* 236; UV (MeOH) λ_{max} 318 mm (ϵ 6300). The exact structure of **6** was established by X-ray crystal analysis: Ryang, H.-S.; Dobrowolsky, D.; Foote, C. S., to be published.

[14] Compound **7**: mp 111 °C dec; ^1H NMR ($CDCl_3$), 1.08 (9 H, s), 3.10 (1 H, dd, J = 2.9, 0.7 Hz), 3.50 (3 H, s), 5.06 (1 H, d, J = 2.9 Hz), 6.09 (1 H, d, J = 0.7 Hz); mass spectrum, *m/e* 224 (M - 44), 208; IR (Nujol) 1760, 1600 cm^{-1}; positive peroxide test with KI/HCl. Ando et al. have isolated this cyclic peroxide from photooxygenation of **1** in MeOH and determined the structure by X-ray crystallography.[19] The above analytical data for **7** are identical with those reported by them.

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[16] (a) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359. (b) Saito, I.; Matsuura, T. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds; Academic Press: New York, 1979; p 511.

[17] ^1H NMR of **1**: δ ($CDCl_3$) 1.25 (9 H, s), 1.35 (9 H, s), 7.49 (1 H, d, J = 2.0 Hz), 7.56 (1 H, d, J = 2.0 Hz). ^1H NMR of **8**: δ ($CDCl_3$) 1.19 (9 H, s), 1.23 (9 H, s), 6.20 (1 H, d, J = 2.3 Hz), 6.87 (1 H, d, J = 2.3 Hz).

[18] (a) Huisgen, R.; Gleischmann, R. *Liebigs Ann. Chem.* **1959**, *623*, 47. (b) Ried, W.; Wagner, K. *Ibid.* **1965**, *681*, 45.

[19] We thank Professor Ando for a prepublication copy of his manuscript: Ando, W.; Miyazaki, H.; Veno, K.; Nakanishi, H.; Sakurai, T.; Kobayashi, K. *J. Am. Chem. Soc.*, preceding paper in this issue.

Dinucleating Octaaza Macrocyclic Ligands from Simple Imine Condensations

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Macrocyclic ligands which are capable of incorporating two metal ions[1] offer the possibility of studying unusual electronic and chemical properties which depend upon proximity of two metal centers. An advantage of macrocyclic systems for this type of investigation is that variation of ring size or other geometric constraints should allow the separation and disposition of the two metal ions to be controlled in a systematic manner. In this paper we describe a series of such ligands which have been obtained in high yields from simple imine condensation reactions and have been characterized by field desorption mass spectrometry and X-ray structure determination.

We have reported[2] that under appropriate conditions the dialdehyde **1a** can be condensed with a range of diamines **2** to give tetraaza macrocycles **3** with a wide range of ring sizes. These reactions proceed without addition of "metal-ion templates",[3] provided that reaction conditions and solvents are selected which allow the free ligands to separate from solution before they can undergo conversion to species which are less soluble or thermodynamically more stable. It was noted,[2] for example, that on prolonged heating in methanol, **3a** is converted to a species of higher relative molecular mass (m_r). We have now characterized a number of the higher m_r materials obtained from condensations under conditions defined in Scheme I and shown them to be an

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[1] (a) Groh, S. E. *Isr. J. Chem.* **1976**, *15*, 227-307. (b) Fenton, D. E.; Lintvedt, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 6367-6372. (c) Fenton, D. E.; Bresciani-Pahor, N.; Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Chem. Commun.* **1979**, 39-40. (d) Gagné, R. R.; Henling, L. M.; Kistenmacher, T. J. *Inorg. Chem.* **1980**, *19*, 1226-1231. (e) Burnett, M. G.; McKee, V.; Nelson, S. M.; Drew, M. G. B. *J. Chem. Soc., Chem. Commun.* **1980**, 829-831. (f) Kahn, O.; Morgenstern-Badarau, I.; Audiere, J. P.; Lehn, J. M.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5936-5938. (g) Coughlin, P. K.; Lippard, S. J.; Martin, A. E.; Bulkowski, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 7616-7617.

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