mg, 0.3 mmol) was stirred for 5 h at room temperature. After pouring into water (20 mL), extracting with $CHCl_3$ (10 × 2 mL), drying, and evaporation of the solvent, TLC and NMR showed the presence of only (*E*)-**9**, with no trace of (*Z*)-**9**. Crystallization from ethanol gave (*E*)-**9** (30 mg, 50% recovery), mp 129 °C.

**Reaction of (*E*)-3 with Sodium Methoxide.** A solution of (*E*)-**3** (1 g, 2.8 mmol) and NaOMe (4.3 mmol, prepared from 100 mg (4 mmol) of Na) in MeOH (3 mL)–MeCN (50 mL) was stirred in the dark at room temperature for 140 h. It was then poured into 1 N HCl (100 mL), extracted with $CHCl_3$ (2 × 50 mL), and the organic phase was separated, washed with $Na_2S_2O_3$ solution and then with water, dried, and evaporated. The $^1H$ NMR showed two MeO signals in 7:3 ratio. If the low field signal is ascribed to a MeO trans to a phenyl group then the products are 7:3 (*Z*)-**12** to (*E*)-**12**. Few additional small MeO signals were observed. Crystallization from cyclohexane gave, as a first fraction, white crystals (30 mg, 4%) mp 203 °C, of 1,2-dimethoxy-1,2-diphenylethylene **13**: $\lambda_{max}$ (EtOH) 224 nm ($\epsilon$ 8900), 255 sh (3600); $\delta$ ($CDCl_3$) 3.27 (3 H, s, MeO), 6.90–6.94 (2 H, m, Ar), 7.22–7.32 (6 H, m, Ar), 7.47–7.50 (2 H, m, Ar); MS, *m/z* 240 (3, M), 165 (10), 151 (100), 105 (63, $PhCO^+$), 91 (11, $C_7H_7^+$), 77 (44, Ph). Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.66. Found: C, 80.24; H, 6.82.

Slow crystallization of the remainder (0.41 g, 56%) from cyclohexane or EtOH and further crystallization from $CH_2Cl_2$ gave long crystals, mp 82 °C, 6:4 (*Z*)-**12** to (*E*)-**12**. The solid obtained from EtOH, mp 83 °C, has the following characteristics: TLC (silica) 6:4 $CH_2Cl_2$–hexane) $R_f$ 0.45; HPLC $R_f$ 7.0 min (silica 60, $CH_2Cl_2$, $F = 1.0$, UV = 254); the two isomers were not separated; $\lambda_{max}$ (EtOH) 246 sh nm ($\epsilon$ 5800), 267 (7300); $\delta$ ($CDCl_3$) 3.47 ((*E*)-**12**), 3.60 ((*Z*)-**12**) [3 H, 2 s, MeO, 7:3 ratio], 7.13–7.47 (10 H, m, Ar); MS, *m/z* 255 (85, M), 194 (91, M – NO – OMe), 180 (18, M – NO – OMe – $CH_2$), 166 (82, M – NO – COOMe), 165 (86, M – $NO_2$ – Me – CO), 151 (9), 136 (14), 119 (22, $PhCOCH_2$), 105 (100, PhCO). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.19; N, 5.49. Found: C, 70.48; H, 5.36; N, 5.08.

When the same reaction was conducted in MeOH for 24 h, to which MeCN was added, and the reaction continued for an additional 24 h, only (*E*)-**3** was recovered, and traces of the product were observed.

**Acknowledgment.** We are indebted to Dr. S. Cohen for the X-ray diffractions, to Prof. H. Schwarz for the mass spectra of **11**, and to the Israel Commission for Basic Research, The israel Academy for Sciences and Humanities, who supported this work.

**Registry No.** (*E*)-**3**, 55902-54-0; (*E*)-**5**, 50460-72-5; (*Z*)-**5**, 19881-68-6; **6**, 52979-79-0; (*E*)-**7**, 96746-49-5; (*Z*)-**7**, 96746-50-8; (*E*)-**8**, 96746-51-9; (*Z*)-**8**, 96746-55-3; (*E*)-**9**, 96746-52-0; (*Z*)-**9**, 96746-53-1; **10**, 838-41-5; **11**, 96746-54-2; (*E*)-**12**, 96746-56-4; (*Z*)-**12**, 96746-57-5; **13**, 30928-28-0; NaOMe, 124-41-4; desoxybenzoin, 451-40-1; sodium *p*-toluenethiolate, 657-84-1; sodium *p*-cresolate, 1121-70-6; sodium azide, 26628-22-8; tetrabutylammonium chloride, 1112-67-0.

**Supplementary Material Available:** Tables S1–S16 giving the crystallographic data (bond lengths and angles, positional, and thermal parameters) for (*E*)-**7**, (*E*)-**9**, **10** and **11** and Figures S1–S4 giving their stereoscopic views (26 pages). Ordering information is given on any current masthead page.

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# Photooxygenation of Acetone Hydrazone: Characterization of an Unstable Intermediate

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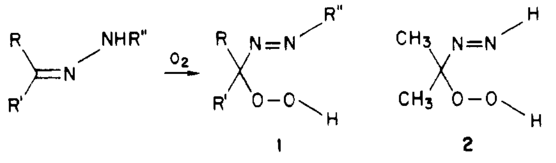
The tetraphenylporphyrin-sensitized photooxygenation of acetone hydrazone produces 2–4% of an unstable compound with a $^1H$ NMR spectrum consisting of singlets at 1.3 (6 H), 13.7 (1 H), and 15.8 (1 H) ppm. The structure assigned is that of the hydroperoxy diazene (azo hydroperoxide) $(CH_3)_2C(OOH)N{=}NH$. The compound decomposes very rapidly above –20 °C with a high yield of formation of $N_2$ but no $O_2$ ($[N_2]:[O_2] > 100:1$). Photooxygenation of either acetone hydrazone or benzophenone hydrazone in toluene gives 10–20% yields of cresols.

The photosensitized oxygenation of hydrazones leads to $\alpha$-azo hydroperoxides **1**.[1,2] These compounds are of interest as radical initiators,[3] as oxidizing agents,[4-6] and as a source of the hydroxyl radical in anhydrous organic media.[7-9] A number of other aspects of their chemistry have been studied, including their structure and spectra,[10-18] formation via autoxidation,[18-20] formation via reaction pathways involving singlet oxygen,[21-23] reactions



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(1) Hiatt, R. In "Organic Peroxides"; Swern, D., Ed.; Wiley: New York, 1971; Vol. II, pp 1–151.

(2) Karnojitzky, V. *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 121–144.

(3) (a) Schulz, M.; Missol, U. *J. Prakt. Chem.* **1980**, *322*, 417–422. (b) MacLeay, R. E.; Sheppard, C. S. U.S. Patent 4010152, 1977; *Chem. Abstr.* **1977**, *86*, 156228s.

(4) Tosi, G.; Passalacqua, V.; Marchetti, L. *Ann. Chim. (Rome)* **1971**, *61*, 5–12.

(5) (a) Landis, M. E.; Lindsey, R. L.; Watson, W. H.; Zabel, V. *J. Org. Chem.* **1980**, *45*, 525–527. (b) Baumstark, A. L.; Vasquez, P.C. *Tetrahedron Lett.* **1983**, *24*, 123–126 and references therein. (c) Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* **1983**, *48*, 65–69.

(6) Osei-Twum, E. Y.; McCallion, D.; Nazran, A. S.; Panicucci, R.; Risbood, P. A.; Warkentin, J. *J. Org. Chem.* **1984**, *49*, 336–342.

(7) Tezuka, T.; Narita, N.; *J. Am. Chem. Soc.* **1979**, *101*, 7413–7415.

(8) (a) Tezuka, T.; Narita, N.; Ando, W.; Oae, S. *J. Am.Chem. Soc.* **1981**, *103*, 3045–3049. (b) Tezuka, T.; Ichikawa, K.; Marusawa, H.; Narita, N. *Chem. Lett.* **1983**, 1013–1016.

(9) Grant, R. D.; Rizzardo, E.; Solomon, D. H. *J. Chem. Soc., Chem. Commun.* **1984**, 867–868.

(10) Pausacker, K. H. *J. Chem. Soc.* **1950**, 3478–3481.

(11) Criegee, R.; Lohaus, G. *Chem. Ber.* **1951**, *84*, 219–224.

(12) Karabatsos, G. J.; Taller, R. A. *J. Am. Chem. Soc.* **1963**, *85*, 3624–3629.

(13) Yao, H. C.; Resnick, P. *J. Org. Chem.* **1965**, *30*, 2832–2834.

(14) Bellamy, A. J.; Guthrie, R. D. *J. Chem. Soc.* **1965**, 2788–2795.

(15) Buckingham, J.; Guthrie, R. D. *J. Chem. Soc. C.* **1967**, 2268.

(16) Lewis, G. E.; Spencer, G. L. *Aust. J. Chem.* **1975**, *28*, 1733–1739.

(17) Schulz, M.; Mostafa, M. A. E.-Z. *Z. Chem.* **1979**, *19*, 210–211.

(18) Nishinaga, A.; Tomita, H.; Oda, M.; Matsuura, T. *Tetrahedron Lett.* **1982**, *23*, 339–342.

(19) Taylor, W. F.; Weiss, H. A.; Wallace, T. J. *J. Org. Chem.* **1969**, *34*, 1759–1761.

(20) Gersmann, H. R.; Bickel, A. F. *J. Chem. Soc. B* **1971**, 2230–2237.

(21) Griffiths, J.; Hawkins, C. *J. Chem. Soc., Perkin Trans. 2* **1977**, 747–752.

(22) Ito, Y.; Kyono, K.; Matsuura, T. *Tetrahedron Lett.* **1979**, 2253–2256.

(23) For related work, see: Friedrich, E.; Lutz, W.; Eichenauer, H.; Enders, D. *Synthesis* **1977**, 893–894.

0022-3263/85/1950-3194$01.50/0

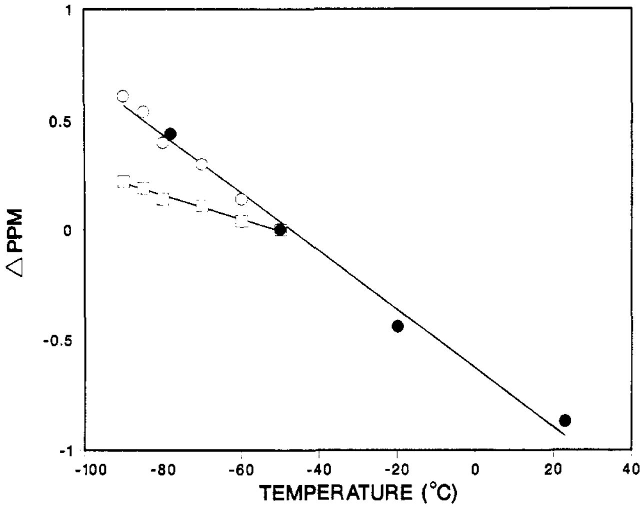


**Figure 1.** Change in chemical shift of the exchangeable peaks of **2** and **3** as a function of temperature ($\delta_T - \delta_{-50\,°C}$): (□) N═NH of **2**; (○) OOH of **2**; (●) OOH of **3**. The chemical shifts in this run at −50 °C are 15.7, 13.4, and 10.35 ppm, respectively.

with reducing agents,[24-27] and base-induced cleavage reactions.[27a,28-30]

For hydrazones with R″ = H, oxygenation would be expected to give a hydroperoxy diazene (azo hydroperoxide) **1** with both OOH and N═NH groups. Such a structure has been proposed[31] but, to our knowledge, never seen. It is expected to be very labile. Decomposition to the ketone, nitrogen, and water is calculated to be exothermic by ~115 kcal mol$^{-1}$. In this paper we report spectral and chemical evidence for the existence of the dimethyl derivative **2**. In addition, we have investigated the photooxygenation of the hydrazones of acetone and benzophenone and present the results of these studies.

## Results

**$^1$H NMR Spectrum.** When a solution of acetone hydrazone and tetraphenylporphyrin (TPP) in $CD_2Cl_2$ at −78 °C was irradiated under a stream of oxygen, an unstable intermediate or intermediates were formed, as indicated by copious evolution of gas as the solution was warmed to ≃−20 °C. The NMR of the solution at −78 °C showed peaks arising from starting hydrazone, azine, acetone, and TPP and four new peaks at approximately 1.3, 11.9, 13.7 (varying from 13.4 to 13.7), and 15.8 (varying from 15.6 to 15.8) ppm. The peaks at 1.3, 13.7, and 15.8 ppm were present in an approximate 6:1:1 ratio. They were assigned to a single compound on the basis of their simultaneous decrease upon repeated cycles of warming to −30 °C and recooling to −78 °C. This compound is assigned the azo hydroperoxide structure **2**. The peak at 15.8 ppm is appropriate for an N═NH resonance,[32] and the peak at 13.7 ppm is assigned to the intramolecularly hydrogen-bonded OOH proton (see Discussion). The peak at 11.9 ppm is unassigned, although its chemical shift and temperature dependence are appropriate for a hydroperoxide group. In some runs its intensity increased as that of the peaks at 13.7 and 15.8 ppm decreased.

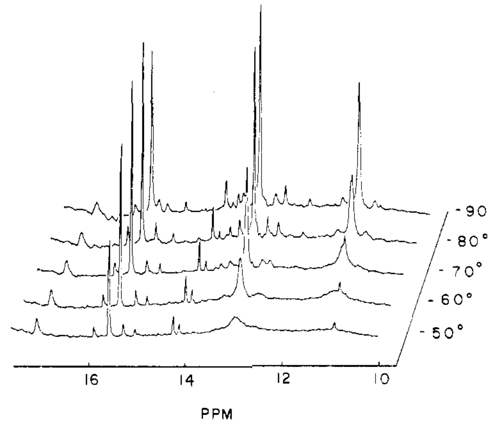
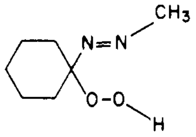


**Figure 2.** TPP-sensitized photooxygenation of acetone hydrazone. $^1$H NMR of the reaction mixture as a function of temperature. In the spectrum run at −50 °C, the peaks at 15.7 and 13.0 ppm are assigned as the N═NH and OOH protons of **2**, respectively.

**Temperature Dependence of the NMR Spectrum.** Chemical shifts of protons bound to nitrogen and oxygen are temperature dependent. For **2**, both the N═NH and OOH resonances shifted upfield as the temperature was raised. The data are shown in Figure 1. The N═NH and OOH resonances shifted 0.06 and 0.13 ppm, respectively, for every 10 °C rise in the temperature. The resonance arising from the OOH proton had the same temperature dependence as that of the hydroperoxide proton of **3**.



**3**

The line widths of the peaks were also temperature dependent (Figure 2). The OOH peak at 13.7 ppm broadened as the solution temperature was raised from −90 to −50 °C. This is probably due to an increasing rate of exchange of the OOH proton. The N═NH peak at 15.8 ppm first narrowed (−80 °C) and then broadened as the temperature was raised to −50 °C. Tsuji and Kosower have shown that the line width of the N═NH resonance in alkyldiazenes is determined in part by quadrupole broadening by the $^{14}N$.[32] Because the N═NH proton also exchanges with other NH and OH protons in solution (vide infra), it is likely that the changes in line width of the peak at 15.8 ppm are due to both $^{14}N$ quadrupole relaxation and exchange effects.

Chemical exchange was probed further by saturation-transfer experiments. Irradiation of the resonance due to the hydrazone $NH_2$ group and water (5.1 ppm, the major source of exchangeable protons) produced a significant decrease in the size of the hydroperoxide peak relative to the azo proton peak. The latter was affected as well, however, indicating that the N═NH group can undergo proton exchange even at −78 °C. Ackerman et al. have shown that the RN═NH moiety can exchange H for D under basic conditions.[33]

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[24] Minisci, F. *Gazz. Chim. Ital.* **1959**, *89*, 626–637.

[25] Witkop, B.; Kissman, H. M. *J. Am. Chem. Soc.* **1953**, *75*, 1975–1980.

[26] (a) Chang, Y.-M.; Profetto, R.; Warkentin, J. *J. Am. Chem. Soc.* **1981**, *103*, 7189–7195. (b) Nazran, A. S.; Warkentin, J. *J. Am. Chem. Soc.* **1981**, *103*, 236–237. (c) Nazran, A. S.; Warkentin, J. *J. Am. Chem. Soc.* **1982**, *104*, 6405–6407.

[27] (a) Schulz, M.; Somogyi, L. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 168. (b) Schulz, M.; Missol, U.; Bohm, H. *J. Prakt. Chem.* **1974**, *316*, 47–53.

[28] Tezuka, T.; Iwaki, M. *Tetrahedron Lett.* **1983**, *24*, 3109–3112.

[29] Tezuka, T.; Iwaki, M.; Haga, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 325–326.

[30] Utaka, M.; Fujita, Y.; Takeda, A. *Chem. Lett.* **1982**, 1607–1610.

[31] Suginome, H.; Uchida, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3225–3231.

[32] (a) Tsuji, T.; Kosower, E. M. *J. Am. Chem. Soc.* **1971**, *93*, 1992–1999. (b) Tsuji, T.; Kosower, E. M. *J. Am. Chem. Soc.* **1971**, *93*, 1999–2004. (c) Kosower, E. M. *Acc. Chem. Res.* **1971**, *4*, 193–198.

[33] Ackerman, M. N.; Hallmark, M. R.; Hammond, S. K.; Roe, A. N. *Inorg. Chem.* **1972**, *11*, 3076–3082.

**Product Yields.** For a given set of reaction conditions, the rate of disappearance of acetone hydrazone varied greatly from run to run. For example, after 5 min of photooxygenation at −78 °C ($CD_2Cl_2$ saturated with $O_2$, [TPP] = $10^{-2}$–$10^{-3}$ M), the amount of remaining acetone hydrazone varied from 12% to 77% (10 runs). The major products of the photooxygenation are acetone and acetone azine. The ratio of these two also varied considerably. In the runs cited above the [acetone]/[acetone azine] ratio varied from 0.2–25. The yields of **2** as measured by $^1H$ NMR ranged from 1–7% (generally 2–4%, 2–14% based on unreacted hydrazone, 20 runs).

The rate of disappearance of **2** was exceedingly variable. For example, one run gave a $\tau_{1/2}$ of ~3.5 h at −50 °C and another gave a $\tau_{1/2}$ of ~4 h at −30 °C. Purging the solution with argon before warming did not improve the reproducibility. The variability of these runs is not surprising because both the diazene and the hydroperoxy groups are very susceptible to induced decomposition.[1,6,9,32,34–36]

**Azine Formation.** The yield of acetone azine generally increased as the temperature of the reaction mixture was raised, probably due to the condensation of product acetone with starting hydrazone. However, control experiments showed that the rate of formation of acetone azine in the low-temperature photooxygenation reactions was substantially higher than could be accounted for by the condensation reaction. It has long been noted that oxidations designed to produce the diazo compound from the hydrazone often give azine as well.[37] The mechanism of azine formation has been postulated to involve attack of one diazo compound on another or formation of a tetrazene followed by loss of $N_2$. Either of these pathways would explain the formation of azine at low temperature in our photooxidations.

**Gas Evolution.** As discussed above, warming of a solution of **2** from −78 °C produced copious gas evolution, beginning at $\simeq$−20 °C. Quantitative measurements showed that the nitrogen yield was 2–7% (6–14% based on unreacted hydrazone, 6 runs). In view of the possibility that **2** might decompose via a retroene reaction, to give oxygen and the starting hydrazone, the oxygen to nitrogen ratio in the evolved gas was measured by GC. The $[O_2]$:$[N_2]$ ratio was less than 1:100, indicating that the decomposition pathways of **2** do not produce $O_2$ as a product.

**Other Photooxygenation Conditions.** Because the yield of **2** was so low in the TPP-sensitized photooxygenation reaction, a number of other sensitizers and conditions were investigated to try and increase the conversion of acetone hydrazone to **2**. Although TPP proved to be the best sensitizer of those investigated, changes in sensitizer and conditions altered the course of the reaction. These experiments are outlined very briefly below. Each set of conditions was investigated 2–4 times. It must be remembered, however, that there are a large number of processes competing in these reactions and that both conversion times and product yields were extremely variable.

Two other singlet oxygen sensitizers were tried: polymer-bound rose bengal and methylene blue. The former induced the oxidation of acetone hydrazone ($CD_2Cl_2$ at −78 °C), but no **2** was formed. The latter was not effective as a photosensitizer; acetone hydrazone remained essentially unchanged after 15 min photooxygenation at 0 °C ($CH_2Cl_2$).

We also investigated TPP with 1,4-diphenylbutadiene (DPBD) as a cosensitizer. The 2 + 4 cycloaddition of DPBD with $^1O_2$ has been used in competition studies to monitor relative rates of addition of $^1O_2$.[38] We have found that the addition of DPBD alters the time course and product yields of amine photooxidations.[39] In the photooxygenation of acetone hydrazone, for example, the reaction proceeded to give a small amount of **2** and acetone. No acetone azine was formed, even at 100% conversion.

Three inhibitors were investigated. β-Carotene and 1,4-diazabicyclo[2.2.2]octane quench singlet oxygen, and 2,6-di-*tert*-butyl-4-methylphenol (BHT) inhibits radical chain reactions. None of them produced any dramatic change in the course of the reaction.

Dicyanoanthracene (DCA) was also investigated. It is known to catalyze photooxidations via electron-transfer and singlet oxygen pathways.[40] Photooxidation using DCA in toluene gave a low to moderate conversion of acetone hydrazone to acetone and the azine after 30–60 min at 0 °C. DCA in $CDCl_3$ was ineffective as a sensitizer. Essentially no reaction was observed after 20 min at 0 °C. The addition of biphenyl[41] in the $CDCl_3$ experiments did not increase the conversion.

It appears from the studies above that $^1O_2$ alone is not enough to oxidize acetone hydrazone. Earlier studies have shown that azo hydroperoxides are formed in both radical chain[10,11,14,18–20] and $^1O_2$ (ref 21–23) reactions.

**Benzophenone Hydrazone Photooxygenation.** Photooxygenation of benzophenone hydrazone at low temperature produced a mixture that did not show any resonances appropriate for the azo hydroperoxide. This may indicate that it did not form or that the rate of decomposition was greatly enhanced by the phenyl groups. No benzophenone azine was produced in the photooxygenation.

The reaction was run under both oxygen and air, and it was found that the reaction rate was approximately 1.6 times faster under oxygen (reaction followed by the appearance of benzophenone in the infrared spectrum). Previous studies have found that hydrazone oxidation is first order in oxygen when the reaction is not photocatalyzed.[19] Our work shows that for the TPP-sensitized reaction, the dependence on oxygen concentration is less than first order. This indicates that radical or radical ion pathways are important. It also indicates that the reaction does not proceed only via singlet oxygen. Reactions that proceed via singlet oxygen usually have rates that are independent of the concentration of $O_2$ in the air to pure oxygen range.[42,43]

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(34) Evanochko, W. T.; Shevlin, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 6428–6432.

(35) Casewit, C. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 4057–4062.

(36) Howard, J. A. In "The Chemistry of Peroxides"; Patai, S., Ed.; Wiley-Interscience: New York, 1983; pp 235–258.

(37) Smith, P. A. S. "Derivatives of Hydrazine and Other Hydronitrogens Having N-N Bonds"; Benjamin/Cummings: Reading, MA, 1982; pp 219–221.

(38) Landis, M. E.; Madoux, D. C. *J. Am. Chem. Soc.* **1979**, *101*, 5106–5107.

(39) Dixon, D. W., unpublished results.

(40) Araki, Y.; Dobrowolski, D. C.; Goyne, T. E.; Hanson, D. C.; Jiang, Z. Q.; Lee, K. J.; Foote, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 4570–4575 and references therein.

(41) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Rahman, A. F. M.; Oliver, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6087–6088 and references therein.

(42) (a) Gollnick, K. In "Advances in Photochemistry"; Noyes, W. A., Jr., Hammond, G. S., Pitts, J. N., Jr., Eds.; Wiley: New York, 1968; Vol. 6, pp 1–122. (b) Foote, C. S. In "Singlet Oxygen, Reactions with Organic Compounds and Polymers"; Ranby, B., Rabek, J. F., Eds.; Wiley: New York, 1978; pp 135–146.

(43) (a) Davidson, R. S.; Goodwin, D.; Pratt, J. E. *Tetrahedron* **1983**, *39*, 2373–2379. (b) Mizuno, K.; Hiromoto, Z.; Ohnishi, K.; Otsuji, Y. *Chem. Lett.* **1983**, 1059–1060. (c) Spada, L. T.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 391–393.

Table I. Yields of Toluene Hydroxylation Products

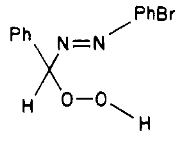
| entry | reactions (temp, °C) | % PhCHO | % $PhCH_2OH$ | % cresols | % cresol isomer distribution ortho | meta | para |
|---|---|---|---|---|---|---|---|
| 1 | acetone hydrazone, TPP (0) | 0.5 | 1.0 | 10 | 44 | 12 | 44 |
| 2 | acetone hydrazone, TPP (−78[a]) | 0.004 | 0.013 | 0.08 | 29 | 11 | 60 |
| 3 | benzophenone hydrazone, TPP (0) | 1.1 | 4.3 | 18 | 52 | 15 | 33 |
| 4 | benzophenone hydrazone, DCA (0) | <0.1 | <0.4 | 3.6 | 42 | 19 | 39 |
| 5 | benzophenone hydrazone, P-RB (0) | 1.0 | 3.0 | 10.8 | 45 | 17 | 38 |
| 6 | photochemical decomposition of 4[b] | | | 6 | 44 | 40 | 16 |

[a] Oxidation was run at −78 °C in $CH_2Cl_2$, toluene was added, and the solution was warmed to room temperature. [b] Reference 8.

**1,1,1-Trifluoroacetone Hydrazone Oxidation.** A $CF_3$ group might stabilize the azo hydroperoxide moiety in one of two ways. First, the $CF_3$ group slightly destabilizes a radical at the α-position and thus should slow the rate of a homolytic scission involving the C–N or C–O bonds.[44–46] Second, the electron-withdrawing nature of the $CF_3$ group would reduce the rate of a heterolytic decomposition of the azohydroperoxide to give $R_2C{=}N^+{=}NH$ and $^-OOH$.[47] To attempt to exploit this stabilizing effect, we synthesized the azo hydroperoxide from the hydrazone of 1,1,1-trifluoroacetone. Photooxygenation of the hydrazone at 0 °C for 45 min gave ~1% of peaks consistent with the desired azo hydroperoxide. Thus, it appeared that the fluorine substituents did stabilize the azo hydroperoxide moiety. However, the yield of desired product was still very low, so this approach was not pursued further. The photooxygenation also gave an approximately 15% conversion of starting material to a substance showing singlets at 1.60 and 6.11 ppm in the $^1H$ NMR. The peak at 1.60 ppm is consistent with a $CH_3(CF_3)(C)(O)O$ or $CH_3(CF_3)C(O)N$ moiety,[48] but the structure was not assigned.

**Oxidation of Toluene.** The ability of **2** to oxidize a substrate was probed by running the oxygenation in the presence of toluene and measuring the yields of oxidized products. The data are given in Table I.

Three points are noteworthy. First, the yield of cresols in the reaction run in toluene (10%, Table I, entry 1) appears substantially higher than the yield in the reaction where **2** was generated in $CH_2Cl_2$ at −78 °C, toluene added, and the solution allowed to warm to room temperature (0.08%, entry 2). However, compound **2** was present generally as only 2–4% of the reaction mixture whenever the amount was measured by $^1H$ NMR. Assuming that the amount of **2** present was 2–4% and that cresols arise only from **2**, then the cresol yield of 0.08% based on starting hydrazone was 2–4% of the amount of **2** present in the reaction mixture when the toluene was added. This calculated cresol yield is a factor of approximately 3 lower than the 10% yield found in the photooxygenation reaction of acetone hydrazone in toluene (entry 1) and a factor of approximately 2 lower than the 6–7% yield of cresols observed by Tezuka et al. in the photodecomposition of **4** (entry 6).



**4**

Second, the ortho:meta:para ratios of the cresol products are 44:12:44 in the experiments run in toluene but 29:11:60 in the experiment run by adding toluene to **2** in $CH_2Cl_2$. It is difficult to compare these ratios meaningfully, because in the latter experiment the intermediate(s) decomposed as the solution was warmed to room temperature. Thus, neither the temperature nor the concentration(s) of the intermediate(s) was constant in this experiment. Both of these factors might affect the isomer ratio.

Finally, for the benzophenone hydrazone oxidations, the cresol isomer ratios were independent of the sensitizer [TPP, polymer-bound rose bengal (P-RB) or dicyanoanthracene (DCA)]. The overall percents of oxidized products were not the same, however, decreasing in the order TPP > P-RB > DCA. Rose bengal is usually considered to be a singlet oxygen sensitizer, although it does participate in electron-transfer processes.[49] DCA can catalyze photooxidation via electron transfer or via singlet oxygen formation.[40] Although the mix of electron transfer and $^1O_2$ chemistry is unlikely to be the same for these sensitizers, the cresol product ratios are similiar. The simplest explanation is than an intermediate(s) is produced via both electron-transfer and $^1O_2$ pathways and that decomposition of this intermediate leads to oxidation of the toluene. This explanation is consistent with the kinetics of oxidation of benzophenone hydrazone under $O_2$ and air described above.

## Discussion

**Structure.** The properties of the unstable intermediate produced upon photooxygenation of acetone hydrazone are most consistent with the hydroperoxy diazene **2**. In the $^1H$ NMR, the peak at 15.8 ppm is appropriate for an N=NH resonance. Kosower and co-workers have studied diazenes RN=NH and have found N=NH chemical shifts at 15.6–16 ppm (e.g., the $CH_3N{=}NH$ peak in $CD_3CN$ at −48 °C is at 15.8 ppm).[32]

The peak at 13.7 ppm is assigned to the hydroperoxide proton. In general, hydroperoxides have OOH resonances between 7.6 and 9.2 ppm. However, intramolecular hydrogen bonding produces a downfield shift.[50] For example, α-hydroperoxypyrazoles **5** have OOH resonances between

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(44) The CH bond-dissociation energies of $CF_3CH_3$ and $CH_3CH_3$ are ~106 (ref 45) and 98 kcal $mol^{-1}$, respectively.

(45) Rogers, A. S. In "Fluorine-Containing Free Radicals"; Root, J. W., Ed.; American Chemical Society: Washington, DC, 1978; ACS Symp. Ser. No. 66, pp 296–313.

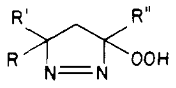
(46) For related work, see: Singh, H.; Tedder, J. M. *J. Chem. Soc.* **1964**, 4737–4741.

(47) Related equilibria are found in the hydration constants of substituted acetones (aqueous solution at 25 °C): acetone, 1.4 × $10^{-3}$, 1,1,1-trifluoroacetone, 35; hexafluoroacetone, 1.2 × $10^6$. Guthrie, J. P. *Can. J. Chem.* **1975**, *53*, 898–906 and references therein.

(48) (a) The peak at 1.60 ppm has a similar shift to that of the hydrate of 1,1,1-trifluoroacetone in $D_2O$ ($CH_3(CF_3)C(OH)_2$, 1.59 ppm), as shown by Buschmann and co-workers.[48b] The chemical shifts for the ketone and hydrate reported by Buschmann and co-workers are apparently reversed. The assignment of 2.38 ppm for the ketone and 1.59 ppm for the hydrate are consistent with the reported chemical shifts for other halogenated ketones, for which the hydrates resonate approximately 0.8 ppm upfield of the respective ketones. (b) Buschmann, H.-J.; Füldner, H.-H.; Knoche, W. *Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 41–44.

(49) (a) Davidson, R. S.; Trethewey, K. R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 169–173, 173–178, 178–182. (b) Davidson, R. S.; Trethewey, K. R. *J. Chem. Soc., Chem. Commun.* **1975**, 674–675.

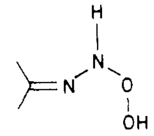
(50) Davis, J. C., Jr.; Deb, K. K. *Adv. Magn. Reson.* **1970**, *4*, 201–270.



**5**

7.2 and 7.8 ppm,[5] whereas linear $\alpha$-azo hydroperoxides (1) have OOH resonances between 8.8 and 10.7 ppm.[13,15,17,26,27b] Hydroperoxides that can form intramolecular hydrogen bonds to nitrogen have a range of chemical shifts from 8.8 to 14.4 ppm.[51-53] Thus, an OOH resonance at 13.7 ppm is at the downfield end of the range of the literature examples of OOH intramolecularly hydrogen bonded to nitrogen. The 2–5 ppm downfield shift of the OOH proton of **2** relative to other intramolecularly hydrogen-bonded azo hydroperoxides may reflect hydrogen bonding to an N=NH rather than an N=NR moiety.

An alternate structure that would display three singlets in a 1:1:6 ratio is the hydroperoxyhydrazone **6** (assuming that the two methyl resonances are coincidentally equivalent).[54] Assignment of the 13.8 ppm resonance as that of an NOOH proton has precedence in the spectra of hydrotrioxides, ROOOH, where the resonance is found in the 12.5–13.7 ppm region.[55-58] However, the monosubstituted hydrazone NH resonance is generally found in the 6.5–8.8 ppm region.[12] The presence of additional neighboring lone pairs in the molecule is expected to shift the resonance downfield but, in the absence of intramolecular hydrogen bonding, not as far as 15.8 ppm. The chemical shifts as a function of temperature are also in accord with assignment of the peak at 15.8 ppm as the NH and that at 13.7 ppm as an intramolecularly hydrogen-bonded OOH resonance. In addition, the nitrogen evolution studies indicate that structure **6** is unlikely. It is difficult to envision a decomposition route for **6** that gives a high yield of $N_2$ unless **6** rearranges to **2** and then decomposes.



**6**

**Decomposition of 2.** Azo hydroperoxide **2** has numerous decomposition pathways open to it. As discussed above, the rate of decomposition was extremely variable from run to run, even in the presence of radical inhibitors. It was not possible to determine whether the decomposition was first order, second order, or a more complex order due to chain pathways.

Four points are noteworthy, however. First, the observation of toluene oxidation products argues that part of the material serves as an oxidant. Possibilities for the oxidant include the azo hydroperoxide itself, a hydroxyl radical, a carbonyl oxide, or a dioxirane. All of these have been proposed as intermediates in azo hydroperoxide decompositions under various reaction conditions.[5,7,8,28,29]

Second, a retroene reaction is not a major decomposition pathway; such a route would give $O_2$, and the gaseous product of the reaction was not $O_2$ but $N_2$ ($[N_2]/[O_2] > 100$).

Third, decomposition in part through an ionic pathway cannot be excluded.[59] Irradiation experiments showed that the N=NH protons were exchangeable even at low temperature.[60] The exchange might be either acid- or base-catalyzed, but the instability of alkyldiazenes to acid and their relative stability in the presence of base ($\tau_{1/2}$ of seconds to minutes)[32,33] indicates that isomerization via the anion is more likely. Decomposition of **2** would give $N_2$, acetone, and $OH^-$.

Fourth, no chemiluminescence was seen. If decomposition were to proceed via isomerization to the *cis*-diazene followed by a concerted fragmentation (**2** → acetone + $N_2$ + $H_2O$), $\simeq$115 kcal would be released. This is enough energy to populate the excited state of acetone ($E_s$ = 88 kcal/mol, $E_T \simeq$ 80 kcal mol$^{-1}$).[61] However, highly exothermic reactions need not produce products that cross into the excited-state manifold. In addition, both amines and TPP act as quenchers, and chemiluminescence might not be seen even if excited products were formed.

## Conclusion

Low-temperature TPP-sensitized photooxygenation of acetone hydrazone produces a compound that is assigned the $\alpha$-azo hydroperoxide structure **2**. Compound **2** is, as expected, very unstable, decomposing very rapidly above -20 °C to give $N_2$. Although only 2–4% of the reaction mixture at any time is azo hydroperoxide **2**, the overall yield of oxidized products when hydrazones are photooxygenated in toluene is 10–20%.

## Experimental Section

**Instrumentation.** NMR spectra were obtained on a Hitachi Perkin-Elmer R-24B spectrometer operating at 60 MHz and on a JEOL FX-100 FT NMR spectrometer operating at 99.55 MHz for protons and 25.00 MHz for carbon-13. Chemical shifts are reported with respect to internal $Me_4Si$. Low-temperature and saturation-transfer experiments were run on the JEOL FX-100. IR spectra were obtained on a Perkin-Elmer 283B instrument. Mass spectra were obtained on a Finnigan 3200 GC–MS (quadrupole) instrument operating at 70 eV. Solid compounds were run by direct insertion of a probe into the ion source. Photooxygenations were carried out with a General Electric 400-W high-pressure sodium lamp or a Sylvania 300-W tungsten–halogen lamp. Hydroxylation product analyses were done on a Hewlett-Packard 7570 GLC instrument with thermal conductivity detection. HPLC analyses were run on a Beckman instrument with 254-nm detection (Model 160) using a Whatman Partisil PXS 5/25 column with $CHCl_3$ as the eluting solvent.

**Materials.** Toluene used in hydroxylation experiments was distilled twice; other solvents were reagent grade. Other com-

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(51) Richardson, W. H. In ref 36; pp 129–160.

(52) Rebek, J.; McCready, R. *J. Am. Chem. Soc.* **1980**, *102*, 5602–5605.

(53) Mochizuki, M.; Anjo, T.; Wakabayashi, Y.; Sone, T.; Okada, M. *Tetrahedron Lett.* **1980**, *21*, 1761–1764.

(54) In the oxidation of $R_2C$=NNHR, the hydroperoxyhydrazone structure, as well as the correct azo hydroperoxide structure, was suggested by Pausacker.[10] Fisher and Anselme have suggested structure **6** in related oxygenations: Fisher, W.; Anselme, J.-P. *J. Am. Chem. Soc.* **1967**, *89*, 5312–5313.

(55) (a) Kovač, F.; Plesničar, B. *J. Am. Chem. Soc.* **1979**, *101*, 2677–2681. (b) Kovač, F.; Plesničar, B. *J. Chem. Soc., Chem. Commun.* **1978**, 122–124.

(56) Stary, F. E.; Emge, D. E.; Murray, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 1880–1884.

(57) Pryor, W. A.; Ohto, N.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 3614–3622.

(58) In the limited number of examples studied to date, the chemical shift does not depend strongly upon whether the hydrotrioxide has the ability to form intramolecular hydrogen bonds. However, those examples that can form intramolecular hydrogen bonds sometimes show two OOOH peaks.[55,56]

(59) Ho, T.-L.; Olah, G. A. *Synthesis* **1976**, 611–612.

(60) (a) NH exchange might also occur via hydrogen atom transfer involving two diazenes. This type of mechanism has been proposed to explain the bimolecular decomposition of RN=NH[32,34] and the isomerization of diimide.[35,60b] The first step is a disproportionation. In the case of **2**, either $(CH_3)_2C(OOH)\dot{N}NH_2$ or $(CH_3)_2C(OOH)NH\dot{N}H$ could be formed. These could return to starting materials with exchange of a hydrogen atom or cleave to products. This disproportionation pathway is not that probed in the saturation-transfer experiments, where the protons at 5.1 ppm (hydrazone and $H_2O$) are exchanging with the N=NH proton. (b) Dykstra, C. E. *Ann. Rev. Phys. Chem.* **1981**, *32*, 25–52.

(61) Murov, S. L. In "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 3.

pounds were used as received: 9,10-dicyanoanthracene (DCA) (Pfaltz and Bauer), polymer-bound rose bengal (P-RB) (Polysciences), *N*,*O*-bis(trimethylsilyl)acetamide (Pierce), anhydrous hydrazine (Baker), *meso*-tetraphenylporphyrin (TPP), methylene blue, β-carotene, 2,6-di-*tert*-butyl-4-methylphenol (BHT), 1,4-diphenyl-1,3-butadiene (DPBD), benzophenone, benzophenone hydrazone, and trifluoroacetone (Aldrich).

**Acetone azine** was prepared from acetone and hydrazine hydrate by the method of Day and Whiting:[62] bp 128–131 °C [lit. bp 128–131 °C[62]]; $^1$H NMR ($CD_2Cl_2$) δ 1.80 (s, 6 H), 1.97 (s, 6 H).

**Acetone hydrazone** was prepared from acetone azine and anhydrous hydrazine by the method of Day and Whiting:[62] bp 122–126 °C [lit. bp 122–126 °C[62]]; $^1$H NMR ($CD_2Cl_2$) δ 1.72 (s, 3 H), 1.86 (s, 3 H), 4.7 (br s, 2 H) [lit. ($CCl_4$) δ 1.67 (s, cis $CH_3$), 1.82 (s, trans $CH_3$)[63]].

**Benzophenone azine** was prepared by the method of Barton et al.:[64] mp 163.5–165.5 °C [lit. mp 162–164 °C[64]].

**1,1,1-Trifluoroacetone Hydrazone.** Anhydrous hydrazine (0.72 g 0.022 mol) was added dropwise to 2.51 g (0.022 mol) of 1,1,1-trifluoroacetone at 0 °C [Caution—extremely exothermic!] to yield an unstable white solid identified spectroscopically as 1,2-bis(1-(trifluoromethyl)-1-hydroxyethyl)hydrazine (**10**): mp <60 °C dec; IR ($CDCl_3$) 3440 (w, br), 1960 (m), 2350 (m), 1180 (s), 860 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 1.45 (m, 3 H), 3.4 (br s, 2 H); mass spectrum, *m/e* (relative intensity) 256 ($M^+$, 0.6), 169 (12), 127 (10), 126 (13), 113 (10), 75 (36), 69 (100), 57 (16), 15 (8), 50 (15).

Compound **10** decomposed to a clear oil within a few hours of exposure to air. Distillation afforded an approximately 10% isolated yield of 1,1,1-trifluoroacetone hydrazone with substantial amounts present in higher boiling fractions: bp 59 °C (30 mm) [lit. bp 51 °C (20 mm)[65]]; IR ($CHCl_3$) 3450 (m), 3000 (w), 1627 (m), 1450 (m), 1375 (s), 1270 (w), 1130 (s); $^1$H NMR ($CDCl_3$) δ 1.88 (m, 3 H), 5.6 (br s, 2 H); $^{13}$C NMR ($CDCl_3$, $^1$H decoupled) δ 8.48 (s), 121.5 (q, $J_{^{13}CF}$ = 271 Hz), 134.6 (q, $J_{^{13}CCF}$ = 34 Hz); mass spectrum, *m/e* (relative intensity) 126 ($M^+$, 70), 69 (51), 66 (23), 57 (100), 51 (10).

**1-(Methylazo)cyclohexyl Hydroperoxide (3).** Cyclohexanone methylhydrazone[66] (40 μL, 0.30 mmol) was dissolved in 500 μL of $CD_2Cl_2$ and photooxygenated at 0 °C for 30 min under the conditions listed below for acetone hydrazone: $^1$H NMR ($CD_2Cl_2$, 23 °C) δ 1.2–2.4 (m, 10 H), 3.78 (s, 3 H), 9.5 (br s, 1 H) [lit. ($CCl_4$) δ 1.34 (m, 10 H), 3.94 (s, 3 H), 9.57 (1 H)[27b]].

**Photooxygenation of Acetone Hydrazone.** The azo hydroperoxide **2** was generated directly in a 5-mm NMR tube. Typically, acetone hydrazone (40 μL, 0.50 mmol) and TPP (3 mg, 5 × 10$^{-3}$ mmol) were dissolved in 0.5 mL of $CD_2Cl_2$. The solution was cooled to −78 °C in a dry ice–acetone cold bath in a glass Dewar flask. The solution was irradiated for from 5 to 60 min with a 400-W high-pressure sodium lamp while oxygen was bubbled through by means of a long needle. Control experiments indicated that light, sensitizer, and oxygen were necessary for the rapid oxidation of the hydrazone.

**Photooxygenation of Benzophenone Hydrazone.** Benzophenone hydrazone (25.7 mg, 0.13 mmol) was oxidized for 20 min under the conditions described for acetone hydrazone. Benzophenone was produced in greater than 90% yield ($^1$H NMR); no benzophenone azo hydroperoxide was detected by low-temperature $^1$H NMR. No benzophenone azine was found in a photooxygenation run at 0 °C in $CDCl_3$ (HPLC analysis). [0 °C was used because the higher temperature maximizes azine formation in the photooxygenation of acetone hydrazone.]

**Photooxygenation of 1,1,1-Trifluoroacetone Hydrazone.** 1,1,1-Trifluoroacetone hydrazone (40 μL, 0.40 mmol) was allowed to react at 0 °C under the conditions described above for acetone hydrazone. After 45 min the reaction was stopped, and the NMR tube was immediately cooled to approximately −78 °C in a dry ice-acetone cold bath. Low-temperature $^1$H NMR (−70 °C) revealed approximately 15% conversion to a broad unresolved peak at 1.60 ppm. A corresponding additional peak at 6.11 ppm was tentatively assigned as the NH or OH associated with the compound(s) resonating at 1.60 ppm. Examination of the downfield region revealed approximately 1% yield of a compound assigned as the azo hydroperoxide on the basis of the downfield peaks (15.81 and 12.07 ppm).

**Quantitative Analysis of Evolved Gas.** In a typical experiment, a 10.0-mL aliquot of a 100.0-mL solution of 95% acetone hydrazone (5.00 mL, 0.0622 mol) and TPP (30.0 mg, 0.0488 mmol) in $CH_2Cl_2$ was bubbled with oxygen during irradiation in a dry ice–acetone cold bath for 30 min. The reaction was stopped, and the solution was left undisturbed for 5 min. The reaction vessel was connected in a closed system, via plastic tubing, to an inverted water-filled 100-mL buret in a water bath in such a manner to capture the evolved gas at atmospheric pressure. The cold bath was removed, and the reaction mixture was warmed to room temperature. The amount of gas evolved was measured in the buret, with the yield of gas calculated as the difference between the observed value and the value obtained from control experiments performed in the absence of hydrazone, TPP, and light.

**Qualitative Analysis of Evolved Gas.** Acetone hydrazone (10 mL, 0.12 mol) and TPP (20 mg, 0.033 mmol) were dissolved in 90 mL of methylene chloride. The photooxygenation was run at −78 °C for 1 h. A spherical lump of gum was observed on the end of the needle. The atmosphere above the solution was purged with helium for 10 min. Carbon monoxide was then bubbled through the solution for 15 min. As the mixture was allowed to warm to room temperature, the gum gradually disappeared. Copious evolution of gas was observed in the water bubbler. Oxygen, nitrogen, and carbon monoxide were separated on a 6-ft 4-Å molecular sieve column with 1-mL injections at room temperature. The retention times were 0.9, 1.6, and 5 min, respectively, with a 60-mL He flow rate. Each of three injections indicated the ratio of nitrogen to oxygen to be greater than 100:1.

**Rate of Benzophenone Hydrazone Oxidation: Oxygen vs. Air.** Typically, a 25-mL solution of benzophenone hydrazone (6.064 mmol), TPP (1.2 × 10$^{-5}$ mmol), and 3-heptanone (8.595 mmol) (as internal standard) in chloroform was irradiated at 0 °C while oxygen or air was bubbled through by means of a long needle. Aliquots (approximately 0.5 mL) were taken from the reaction mixture at 1-min intervals up to 10 min. A final aliquot was taken after 20 min. An IR spectrum was taken of each aliquot in the absorbance mode. The peaks were recorded for benzophenone (1650 cm$^{-1}$) and 3-heptanone (1710 cm$^{-1}$). The relative concentrations were determined by comparison of integrated peak areas.

**Hydroxylation of Toluene.** The analysis of the toluene hydroxylation products is based on the procedure of Walling and Johnson.[67] Typically, a 50.00-mL toluene solution of the hydrazone (2.666 mmol) and sensitizer (1.5 × 10$^{-5}$ mmol) was prepared in a volumetric flask. A 10.00-mL aliquot was irradiated at 0 °C while oxygen was bubbled through by means of a long needle. The toluene was removed under vacuum, and the products were dissolved in ethyl ether. The ether solutions were extracted with 0.5 M sodium hydroxide solution (in four protions) to separate the cresols.

To analyze for benzyl alcohol and benzaldehyde, the ether layer obtained above was dried with magnesium sulfate, and the solvent was removed under vacuum. The products were then dissolved in a small amount of ether (typically 2 mL) containing a known amount of biphenyl. This solution was then analyzed for benzyl alcohol, benzaldehyde, and biphenyl by GLC (15-ft column of SE-52 on Chromosorb P, programmed oven temperatures from 75–190 °C, and a He flow rate of 60 mL per min).

To analyze for cresols, the NaOH extract from above was acidified with 12 N HCl, extracted with ether, and dried. The solvent was removed, and the products were dissolved in ether containing a known amount of phenol. Silylation with *N*,*O*-bis(trimethylsilyl)acetamide permitted separation of the cresols by GLC, which eluted in the order ortho, meta, and para under the above conditions. Control experiments performed in the

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[62] Day, A. C.; Whiting, M. C. *Org. Synth.* **1970**, *50*, 3–6.

[63] Karabatsos, G. J.; Osborne, C. E. *Tetrahedron* **1968**, *24*, 3361–3368.

[64] Barton, D. H. R.; O'Brien, R. E.; Sternhell, S. *J. Chem. Soc.* **1962**, 470–476.

[65] Shepard, R. A.; Sciaraffa, P. L. *J. Org. Chem.* **1966**, *31*, 964–965.

[66] Todd, D. *J. Am. Chem. Soc.* **1949**, *71*, 1353–1355.

[67] Walling, C.; Johnson, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 363–367.

absence of hydrazone yielded no detectable hydroxylation products (less than $6 \times 10^{-4}$ of the yield of reactions run as described above).

**Hydroxylation of Toluene in Methylene Chloride.** In a typical reaction, acetone hydrazone (3.00 mL, 0.0373 mol) and TPP (11.2 mg, 0.0182 mmol) were dissolved in methylene chloride, which was diluted to 50.00 mL in a volumetric flask. A 20.00-mL aliquot was removed, precooled to low temperature in a dry ice–acetone cold bath, and reacted by irradiating for 1 h under a stream of oxygen. After 1 h the reaction was stopped, and 20.00 mL of precooled toluene was added to the reaction vessel. The toluene and methylene chloride were removed under vacuum and the products analyzed as described above.

**Attempted Observation of Chemiluminescence.** Acetone hydrazone (2.0 mL, 0.025 mol) and TPP (17 mg, $2.7 \times 10^{-5}$ mol) were dissolved in 50 mL of methylene chloride. A portion (25 mL) of this solution was precooled in a dry ice–acetone cold bath and reacted under the photooxygenation conditions for 30 min. The reaction was stopped, and 25 mL of a precooled solution of diphenylanthracene (8.5 mg, $2.6 \times 10^{-5}$ mol) was added. The solution was allowed to warm to room temperature under observation in a darkened room. In a separate experiment, the remaining 25 mL of the above acetone hydrazone solution was reacted as above. A precooled solution of dibromoanthracene (8.6 mg, $2.6 \times 10^{-5}$ mol) in 25 mL of methylene chloride was added and observed as above. No light was seen in either experiment.

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. The mass spectral facility was support by NIH Grant RR00954 from the Division of Research Resources.

**Registry No.** 1 (R = $CF_3$, R′ = $CH_3$, R″ = H), 97315-16-7; **2**, 97315-14-5; **3**, 50265-80-0; **10**, 97315-15-6; $CH_3C(CF_3)$=$NNH_2$, 6257-45-0; $CF_3C(O)CH_3$, 421-50-1; $PhCH_3$, 108-88-3; PhCHO, 100-52-7; $PhCH_2OH$, 100-51-6; acetone, 67-64-1; acetone azine, 627-70-3; acetone hydrazone, 5281-20-9; hydrazine, 302-01-2; benzophenone azine, 983-79-9; cyclohexanone methylhydrazone, 1567-83-5; benzophenone hydrazone, 5350-57-2; benzophenone, 119-61-9; *o*-cresol, 95-48-7; *m*-cresol, 108-39-4; *p*-cresol, 106-44-5.

# Notes

## 2,5-Disubstituted Benzotricyclo[4.2.1.$0^{2,5}$]nonanes: Photochemical Precursors to Substituted Bridged *o*-Xylylene Derivatives

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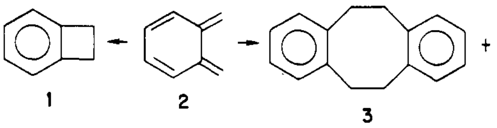
*o*-Xylylene (**2**) is a highly reactive intermediate which has attracted considerable theoretical and experimental attention.[1] This material when generated in fluid solution is unstable both with regard to dimerization and also internal cycloaddition to form dihydrobenzocyclobutene (**1**).



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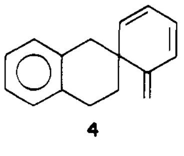

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The electrocyclic ring closure, which presumably occurs via a symmetry allowed conrotatory mode,[2] is particularly interesting, and recently Roth and co-workers[3] have measured the activation energy (29 kcal/mol) for this process by flash photolytic techniques. In this regard, we have previously demonstrated that bridging the *o*-xylylene moiety with a bulky bicyclic group not only prevents dimerization but also inhibits the electrocyclic reaction presumably by forcing a symmetry forbidden disrotatory ring closure.[4] The bridged, bicyclic *o*-xylylene **6** is available by the photolysis of either *exo*- or *endo*-3,4-benzotricyclo[4.2.1.$0^{2,5}$]nonane in rigid media.

There has been considerable theoretical interest recently in the effects of substituents on the rate of electrocyclic reactions. Carpenter and co-workers,[5c,d] using a conceptually simple perturbational approach, have predicted relative substituent effects for a wide variety of pericyclic processes and have further suggested that these effects should be maximized for symmetry forbidden processes. This, coupled with the bimolecular stability of the bicyclic derivative **6**, suggested that substituted derivatives would be ideal candidates for the study of the disrotatory $8\pi$ electrocyclic ring closure. The synthesis of appropriately substituted derivatives of **6** reduces to developing a technique for selectively introducing substituents into positions 2 and/or 5 of the parent tricyclononanes **5** or **7**. We report here our synthetic efforts in this area.

The parent hydrocarbons **5** and **7** have been prepared either by the Diels–Alder cycloaddition of benzocyclobutadiene with cyclopentadiene[6] or by the 2 + 2 cycloaddition of benzyne to norbornene,[7] respectively. Since the former approach seemed to lack synthetic versatility,[8]

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(1) McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270 and references therein.

(2) Woodward, R. B.; Hoffman, R. "The Conservation of Orbital Symmetry", Academic Press: New York, 1970.

(3) (a) Roth, W. R.; Biermann, M.; Dekker, H.; Jochems, R.; Mosselman, C. Hermann, H. *Chem. Ber.* **1978**, *111*, 3892. (b) Roth, W. R.; Scholz, B. P. *Chem. Ber.* **1981**, *114*, 3741.

(4) (a) Miller, R. D.; Kolc, J.; Michl, J. *J. Am. Chem. Soc.* **1976**, *98*, 8510. (b) Steiner, R. P.; Miller, R. D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 1820.

(5) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 1200. (b) Epiotis, N. D. *Angew, Chem., Int. Ed. Engl.* **1974**, *86*, 825. (c) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877. (d) Wilcox, C. F., Jr.; Carpenter, B. K.; Dolbier, W. R. *Tetrahedron* **1979**, *35*, 707. (e) Jensen, A.; Kunz, H. *Theoret. Chim. Acta* **1984**, *65*, 33.

(6) Cava, M. P.; Mitchell, M. J. *J. Am. Chem. Soc.* **1959**, *81*, 5409.

(7) Simmons, H. E. *J. Am. Chem. Soc.* **1964**, *83*, 1657.

(8) Very recently the preparation of 2-chloro-*endo*-3,4-benzotricyclo[4.2.1.$0^{2,5}$]non-7-ene by the Diels–Adler trapping of chlorobenzocyclobutadiene generated in situ has been reported: Ghenciulescu, A.; Georghiu, M. D.; Enescu, L.; Dinulescu, I. G.; Avram, M. *Revue Roumaine de Chemie* **1984**, *29*, 49.

0022-3263/85/1950-3200$01.50/0