temperature, and worked up as described above. GLC analysis (SE-30, 50–200 °C at 40 °C/min) revealed the presence of (0.92 mmol, 92%) 6-dodecanone and 0.95 mmol (95%) of cyclohexanone. No cyclohexanol could be detected.

Acknowledgment. We thank the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (GM 31013) for support of this work. An instrumentation grant from the National Institutes of Health (RR 01709) is also gratefully acknowledged.

Substituent Effects on Nitroxide Hyperfine Splitting Constants

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Substituent effects on the ESR hyperfine splitting constants (hfsc) in a variety of radicals containing substituted phenyl moieties have been investigated.[1-19] In theory, measurements of this type should accurately reflect the changes in electron density due to substituent variation and should, therefore, correlate with the Hammett σ constants;[1,20] in fact, however, only marginal correlations are observed. Since the substituted phenyl moiety was directly bound to a site of high spin density in nearly all of the radical systems studied, some of the deviations have been attributed, quite reasonably, to resonance effects.[1,3] The present report shows that an excellent correlation of nitrogen hfsc can be achieved by using Hammett σ parameters alone when a nitroxide radical center and substituted phenyl moiety are insulated from one another by a saturated carbon atom.

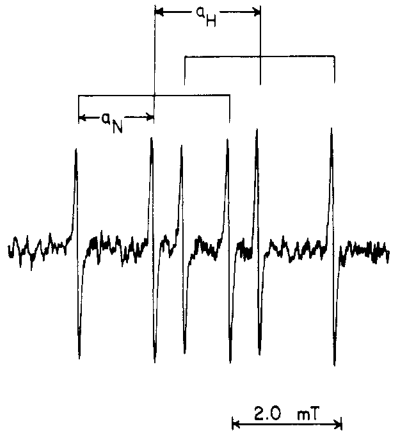


Figure 1. A typical spin adduct ESR spectrum showing the nitrogen and hydrogen hfsc. In this case, the spin adduct is that of the unsubstituted phenyl radical with DMPO. The instrument parameters are as follows: microwave power, 20 mW; modulation frequency, 100 kHz; modulation amplitude, 0.025 mT; gain, 1.25 $\times 10^5$; time constant, 20 ms; scan range, 7.0 mT; scan time, 50 s; number of scans, 3.

Table I. Hyperfine Splitting Constants of Substituted Phenyl Spin Adducts of DMPO in Benzene

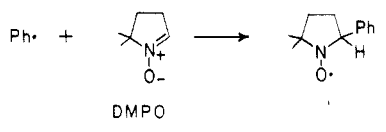
substituent	σ^a	$a_N{}^b$	$a_H{}^b$
p-OCH$_3$	−0.27	1.393 ± 0.002	1.951 ± 0.003
p-CH$_3$	−0.17	1.391 ± 0.003	1.940 ± 0.002
m-CH$_3$	−0.07	1.388 ± 0.003	1.931 ± 0.003
H	0.00	1.382 ± 0.001	1.927 ± 0.002
m-OCH$_3$	0.12	1.383 ± 0.001	1.897 ± 0.002
p-Cl	0.23	1.382 ± 0.002	1.936 ± 0.001
m-Cl	0.37	1.379 ± 0.002	1.924 ± 0.002
m-CF$_3$	0.43	1.377 ± 0.002	1.945 ± 0.004
p-CN	0.66	1.375 ± 0.002	1.930 ± 0.002
m-NO$_2$	0.71	1.373 ± 0.002	1.956 ± 0.004
p-NO$_2$	0.78	1.370 ± 0.003	1.933 ± 0.007

[a] σ substituent constants from: Leffler, J. E.; Grunwald, E. In "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; p 173. [b] In units of mT; deviations expressed as 95% confidence limits, $(t_{0.05,1})$(standard deviation)$/n^{0.5}$.

Results and Discussion

When a benzene solution of phenyl iodide or one of its substituted derivatives and the spin trap 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) is photolyzed in the cavity of an ESR instrument, a six-line spectrum characteristic of a phenyl radical spin adduct of DMPO is immediately observable (see Figure 1 for a typical ESR spectrum). This result can be accounted for by the mechanism shown in eq 1–3. Photolysis causes the rupture of the phenyl–iodine bond, giving a phenyl radical and atomic iodine (eq 1). The phenyl radicals are then rapidly scavenged by the spin trap (eq 2), while the iodine atoms combine (eq 3). Both the

$$\mathrm{Ph{-}I} + h\nu \longrightarrow \mathrm{Ph\cdot} + \mathrm{I\cdot} \qquad (1)$$



(2)

$$2\,\mathrm{I\cdot} \longrightarrow \mathrm{I_2} \qquad (3)$$

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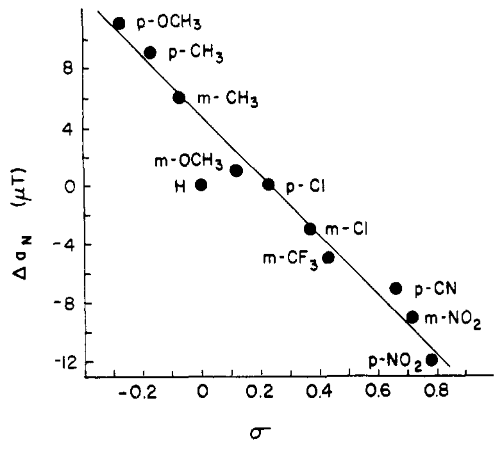
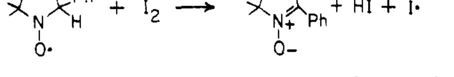


Figure 2. A plot of the Hammett σ constants vs. the difference between the nitrogen hfsc of the substituted phenyl/DMPO spin adducts and that of the unsubstituted spin adduct in μT. The line corresponds to the least-squares fit utilizing all of the data points except that for the unsubstituted species (see text).

nitrogen and hydrogen hfsc values for the unsubstituted nitroxide (see Table I) are in excellent agreement with values (1.376 and 1.988 mT, respectively) reported previously by Janzen and Liu.[21]

An additional complexity is represented by the observation that as photolysis continues and the concentration of molecular iodine formed by eq 3 increases, the nitroxide signal begins to decrease. If the light source is turned off, the nitroxide concentration rapidly goes to zero. This observation can be rationalized by molecular iodine oxidizing the nitroxide to a diamagnetic form. In this respect, the behavior of this nitroxide is markedly different from that reported for di-*tert*-butyl nitroxide, which appeared to be stable to iodine.[22] We suggest that the β-hydrogen present in our system renders this nitroxide much more susceptible to oxidation, possible via an overall scheme such as that depicted by eq 4.



(4)

The nitrogen and hydrogen hfsc obtained for the 11 substituted phenyl spin adducts are given in Table I, along with the corresponding Hammett substituent constants. The plot of the difference between the nitrogen hfsc of the substituted nitroxides and the hfsc of the unsubstituted nitroxide (in μT)[23] vs. Hammett σ parameters is shown in Figure 2. The regression parameters for all 11 points are as follows: slope = −19.6 ± 0.9; intercept = 4.1 ± 1.0; correlation coefficient = 0.95. If the point corresponding to the unsubstituted compound is omitted from the correlation, these regression parameters become −20.5 ± 0.6, 4.8 ± 0.6, and 0.99, respectively. The point corresponding to the unsubstituted phenyl group (i.e., X = H) clearly lies off the line determined by the remaining, substituted species. In marked contrast to the excellent correlation obtained with the nitrogen hfsc data, the correlation of the hydrogen hfsc data with σ show only scatter with no apparent correlation (see Figure 3).

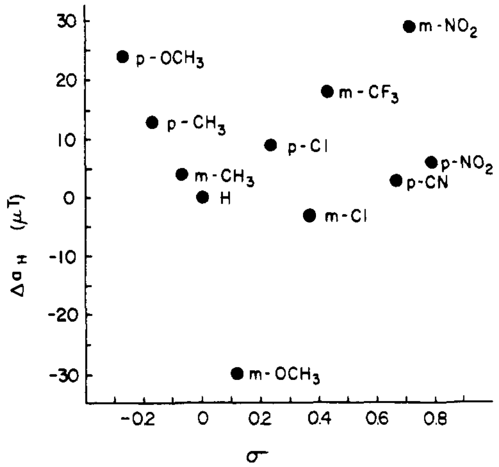
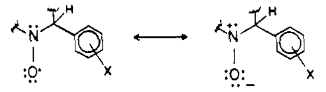


Figure 3. A plot of the Hammett σ constants vs. the difference between the hydrogen hfsc of the substituted phenyl/DMPO spin adducts and that of the unsubstituted spin adduct in μT.

The excellent correlation observed for the nitrogen hfsc with the hammett σ constants can most easily be rationalized in terms of the two contributing structures for the nitroxide radical (**1a** and **1b**). Electron-donating sub-



1a 1b

stituents stabilize form **1b** and thereby increase the spin density on nitrogen; thus, larger nitrogen hfsc are observed.[10] The fact that the correlation utilizing the simple Hammett σ parameters (including both para and meta substituents) is satisfactory suggests that the effect of the substituents is primarily inductive (i.e., electrostatic) in nature.[24] The failure of the unsubstituted species to fit on the line determined by the substituted ones can not be conclusively explained at this time. One possibility is that the σ parameters for all of the substituents, but not hydrogen, include a significant resonance contribution.[25] The substituted compounds might therefore differ from the unsubstituted one if there is a small hyperconjugative interaction between the nitroxide and the phenyl ring. Alternatively, so-called "ponderal" contributions have been noted[26,27] that could have the effect of altering the indirect dipolar interaction between the phenyl and nitroxide moieties.

In view of the excellent correlation between the nitrogen hfsc and σ, the complete lack of any correlation of the hydrogen hfsc data is very intriguing. Our current hypothesis is that there are direct through-space dipole–dipole interactions[27] between the substituents and the benzylic C–H bond that significantly alter the spin density at the hydrogen and, thereby, affect the coupling between that hydrogen and the unpaired electron on the nitroxide nitrogen in an as yet unpredicatable way. With benzene as solvent, the polar N–O moiety may effectively screen the nitroxide nitrogen from the phenyl substituents[28] so that little scatter due to direct dipolar interactions is introduced into the nitrogen data. Interestingly, preliminary experiments with several substituents in Freon-11 suggest that it may be possible to observe direct dipolar effects on

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the nitrogen hfsc as well if the solvent has a sufficiently low effective dielectric constant.

Experimental Section

Sealed ampules of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were obtained from Sigma and used without further purification. The substituted phenyl iodides were obtained from Aldrich (*p*-OCH_3, *m*-CH_3, H, *m*-OCH_3, *p*-Cl, *m*-Cl, *m*-NO_2, *p*-NO_2), ICN (*p*-CH_3), Pierce (*m*-CF_3), or Eastman Kodak (*p*-CN); all of these compounds were used as received. Benzene (Aldrich "gold label") was used without further purification.

A stock solution of DMPO was prepared by dissolving 1.0 g in 100 mL of benzene; this gave a solution having approximately 0.08 M DMPO. Benzene solutions of the substituted phenyl iodides were prepared by dissolving sufficient amounts of each substrate so as to give a concentration of 0.1 M. Reaction mixtures were then prepared by mixing equal volumes of the stock DMPO solution with each of the substituted phenyl iodide solutions. Thus, the final concentrations were 0.04 M DMPO and 0.05 M substituted phenyl iodide. Aliquots (ca. 0.5 mL each) of these reaction mixtures were then transferred to at least six standard ESR tubes, and the solutions were degassed with nitrogen.

The tubes containing the solutions of DMPO and phenyl iodides were then placed in the cavity of the ESR instrument (IBM ER 100D) and continually photolyzed at room temperature with a 200-W Hg source through the radiation grid in the front of the cavity. Typically, three 50-s scans were accumulated for each experiment. Rapid acquisition of the spectra (within 1 min after the start of photolysis) was generally necessary since the molecular iodine resulting from the combination of the iodine atoms formed in eq 1 rapidly quenched the nitroxide spin adducts.

Acknowledgment. I gratefully acknowledge the encouragement and helpful discussions with Professors William A. Pryor and Richard D. Gandour. This work was supported by a grant to W.A.P. by the National Science Foundation (CHE-8303497) and by a contract to W.A.P. from the National Foundation for Cancer Research.

Registry No. DMPO, 3317-61-1; *p*-$MeOC_6H_4I$, 696-62-8; *p*-MeC_6H_4I, 624-31-7; *m*-MeC_6H_4I, 625-95-6; PhI, 591-50-4; *m*-$MeOC_6H_4I$, 766-85-8; *p*-ClC_6H_4I, 637-87-6; *m*-ClC_6H_4I, 625-99-0; *m*-$CF_3C_6H_4I$, 401-81-0; *p*-CNC_6H_4I, 3058-39-7; *m*-$NO_2C_6H_4I$, 645-00-1; *p*-$NO_2C_6H_4I$, 636-98-6; [2,2-dimethyl-5-(*p*-methoxyphenyl)-1-pyrrolidinyl]oxy, 100655-66-1; [2,2-dimethyl-5-(*p*-methylphenyl)-1-pyrrolidinyl]oxy, 100655-67-2; [2,2-dimethyl-5-(*m*-methylphenyl)-1-pyrrolidinyl]oxy, 100655-68-3; (2,2-dimethyl-5-phenyl-1-pyrrolidinyl)oxy, 40936-12-7; [2,2-dimethyl-5-(*m*-methoxyphenyl)-1-pyrrolidinyl]oxy, 100655-69-4; [2,2-dimethyl-5-(*p*-chlorophenyl)-1-pyrrolidinyl]oxy, 100655-70-7; [2,2-dimethyl-5-(*m*-chlorophenyl)-1-pyrrolidinyl]oxy, 100655-71-8; [2,2-dimethyl-5-[*m*-(trifluoromethyl)phenyl]-1-pyrrolidinyl]oxy, 100655-72-9; [2,2-dimethyl-5-(*p*-cyanophenyl)-1-pyrrolidinyl]oxy, 100655-73-0; [2,2-dimethyl-5-(*m*-nitrophenyl)-1-pyrrolidinyl]oxy, 100655-74-1; [2,2-dimethyl-5-(*p*-nitrophenyl)-1-pyrrolidinyl]oxy, 100655-75-2.

Dye-Sensitized Photooxygenation of 1,2-Cyclopentanediones in Methanol

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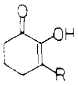
In previous papers,[1] we have reported the dye-sensitized photooxygenation of 1,2-cyclohexanediones (1). The reaction with singlet oxygen has been shown to proceed via an endoperoxide 4, which either liberates carbon monoxide to afford δ-keto acid 2 or is attacked by solvent alcohol to produce α-hydroxyadipic acid monoester 3. Interestingly the product distribution has been found to be highly dependent upon the reaction temperature. The intermediacy of endoperoxide 4 has been discussed on the basis of products 2 and 3, as well as CO and CO_2 liberated.



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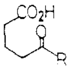

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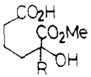

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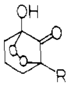

4

On the other hand, 3-methyl-1,2-cyclopentanedione (**5a**) was reported by Wasserman and Pickett[2] to undergo dye-sensitized photooxygenation in the presence of fluoride in chloroform to give 4-oxopentanoic acid (**6a**) with liberation of carbon monoxide. It was considered worthwhile to examine how 1,2-cyclopentanediones (**5**) react with singlet oxygen in alcohol and compare the result with that of **1** to obtain any information about the dye-sensitized photooxygenation.

Results and Discussion

The results of the reaction are listed in Table I. The reaction provides two kinds of products: γ-keto acid **6** with liberation of carbon monoxide and methyl α-hydroxyglutarate **7** presumably formed by trapping the intermediate **8** by methanol. Thus, the reaction path shown in Scheme I can be formulated in the same way as that for 1,2-cyclohexanediones (**1**).[1] The path through the five-membered endoperoxide **8** should be major and the one through the four-membered dioxetane **9** should be minor, as judged from the amount of CO_2 liberated[3] and the yields of **6** and **7** produced. Although the situation seems to be the same, there is a marked difference in the product distribution between **5** and **1**. For the diones **5a** and **5b**, methyl α-hydroxyglutarate **7a** and **7b** were the major products, γ-keto acids **6a** and **6b** being the minor ones or obtained only in trace amounts, whereas, for the diones **1**, δ-keto acids **2** were the major products, methyl α-hydroxyadipates **3** being the minor ones. The very low amounts of CO and CO_2 as shown in Table I also indicate that the major decomposition path of **8** is the trapping by solvent leading to **7**. A rationale to explain the predominance of **7** is as follows. The endoperoxide **8** derived from **5** reacts much more readily with methanol than the endoperoxide **4** derived from **1**, probably owing to the ease with which methanol molecules can approach the carbonyl carbon (Figure 1).

The temperature dependency of the product distribution is observed only for **5a** (Table I), to a lesser extent than that for **1b**.[1] This can be a consequence of the enhanced reactivity of **8**, leading to **7** as discussed above.

An interesting but inexplicable fact is the decreased reactivity of the dione **5** toward singlet oxygen as compared with the dione **1**. From the reaction time and the amount of the dione recovered, it can be concluded that the dione **5** reacts with singlet oxygen several times as slow as the dione **1**. A direct competition of **5a** and **1a** toward singlet oxygen indicated that **5a** reacts with singlet oxygen 5.5

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